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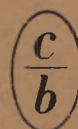
March, 1995

LITHOLOGY AND MINERAL RESOURCES

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IRON AND SULFUR IN THE SEDIMENTARY PROCESS; OXYGEN-ENRICHED BLACK SEA ZONE. Part 1. Fe- and S-Species in Holocene Deposits of Certain Shelf Areas

A. A. Morozov

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Data presented here involve distribution of reactive forms of Fe and of reducing sulfur in Holocene deposits of the Crimean Kalamitsk Shelf, as well as Anatolian and Bulgarian Black Sea shelf areas. Details of the studied distribution characteristics and associated theoretical interpretations are presented.

Behavior of the most important diagenetically active elements during late Quaternary sedimentation on the Black Sea shelf and in the water column of oxidized zones of the sea is the pivotal aspect in complex geochemical Black Sea Basin studies. Numerous factors and theoretical assumptions indicate that processes in which Fe and S compounds participate within the hydrogen sulfide zone greatly influence lithological–mineralogical configuration not only on the shelf but in the entire deep-water basin as well [12, 17, 21]. For this reason, the distribution pattern of the reactive iron and reduced sulfur species in the shelf sediment sequence and results of similar studies of hydrogen sulfide zone deposits [12] provide the necessary data base for understanding geochemical mechanisms that participated in Late Quaternary Black Sea sediment genesis in general.

Distribution patterns in upper horizons of the sediment beds within the hydrogen sulfide zone reflect the profound present-day diagenetic process. It is characterized by intensive redox changes in sediments, accompanied by significant accumulation of reduced forms of certain elements. The alterations represented overall early diagenetic changes in marine sediments, also reflected in Modern Black Sea shelf deposits.

A main research task was to understand multiple physicochemical relationships between depositional conditions and effects of early diagenesis. Their impact on sediment beds is shown by the concentration maxima of the total reduced Fe- and S-species, as well as their ratios in the total reactive Fe and total hydrogen sulfide-sulfur content. Significantly, the well-studied sedimentation conditions during Holocene basin evolution provide a basis for data interpretation. By calculations, we understand early diagenetic processes during deposition of Late Euxinic, Early Black Sea, and Modern units.

Five Holocene sediment cores have been studied. They were obtained on the Kalamitsk shelf, near the Crimea (Station 797, 83 m depth; Sta. 800, 119 m depth, Sta. 795, 150 m depth), the Anatolian shelf (Sta. 822, 99 m depth), and the Bulgarian shelf (Sta. 861, 69 m depth; Fig. 1). The cores were taken in 1984 during the eight-week cruise of R/V *Vityaz'*, by direct-flow drill-corer TBD and dredge *Okean-50* [10].

Components of the sediment samples, including natural moisture content, were determined by traditional analytical methods [5, 19, 20]. Figure 2 shows component concentrations as a ratio of dry carbonate-free matter and of the total reactive Fe content in given beds. The components include nonsulfide forms of bi- and trivalent iron, Fe-pyrite, and acid-soluble Fe-sulfides (hydrotroilite). In addition, the concentration values of pyrite, sulfide, native (elemental), and organic forms of sulfur, CaCO_3 , organic C, was expressed in percentages of the dry sediment volume. The sulfate S-content of muddy waters (mg/ml), the moisture content and potential values (mV) of the platinum electrode (E_p) were also determined in certain cores. The total iron content was analyzed in dried sediments from individual suspendate samples. The difference between total iron and total reactive iron content corresponds to the detrital iron content.

A similar project was undertaken in 1964 on the Kalamitsk shelf on board of R/V *Akademik Vavilov*. Distribution patterns of Fe and S species were studied in three cores. The samples then were taken along a similar, SSW-oriented offshore profile, with comparable depth and thickness values of the sediment units [6-8]. Our data virtually duplicated these, proving the reliability of mapped component distribution patterns and their value in solving timely problems.

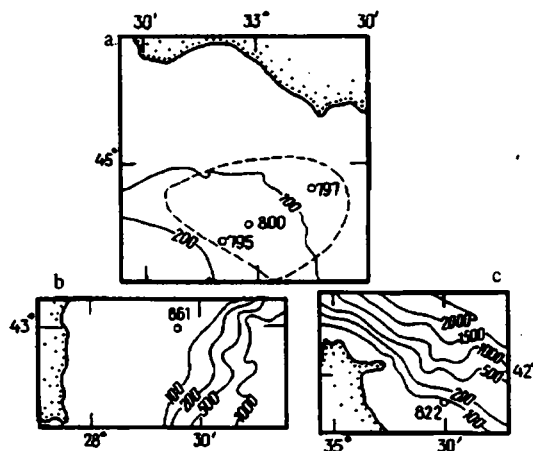


Fig. 1. Sample station locations: a) Kalamitsk Shelf (Sta. 797 – 44° 55.0'N, 33°15.0'E, 83 m depth; Sta. 800 – 44°48.2'N, 32°57'E, 119 m depth; Sta. 795 – 44° 45 5'N, 32°51.3'E, 150 m depth); b) Anatolian shelf (Sta. 822, 41°54.5'N, 35°28.2'E, 99 m depth); c) Bulgarian shelf (Sta. 861, 43°00.6'N, 28°23.2'E, 69 m depth). Dashed lines outline Fe – Mn concretion ("ZhMK")-field.

GENERAL CHARACTERISTICS OF STUDIED SEDIMENTS*

The Kalamitsk shelf cores, taken near the Crimea (Fig. 1a), include the upper interval of the Late Euxinic Horizon and, correspondingly, the entire Early Black Sea and Modern sequence. The Late Euxinic Horizon deposits (H_L) are represented by light-gray, finely dispersed, carbonate and clay-bearing muds, with *Deissensia* shells and their detritus. Only at one station, located in the deepest water (Station 795; 150 m depth) is this unit thick (c. 4 m). The bed was described in a relative study of sediments of the hydrogen sulfide zone [12]. Beds, enriched in hydrotroilite, composed of acid-soluble iron sulfides, occur in the 300-315- and 435-440-cm intervals of the lower core section. The upper interval in all Late Euxinic deposits of this region displays a sharp lithologic contact toward directly overlying Early Black Sea period muds.

In contrast with thick sapropelic deep basin deposits, the Early Black Sea Horizon (H_{II}) is very poorly represented on the Kalamitsk shelf. It appears as a vaguely defined sapropelic bed. A greatly condensed, c. 44-cm clayey-carbonate-bearing, homogeneous, greenish-gray mud horizon in core at Station 795 (150 m depth) does not display lithological boundaries. The same uniform mud occurs as a 235-cm, post-Late Euxinic horizon at shallow-water Station 797 (83 m). Here, however, it displays uneven hydrotroilitic pigmentation. Minor lithological differences between Early Black Sea and Modern deposits were found only in core at intermediate Station 800 (119 m depth).

The Anatolian shelf core from Station 822 was taken between Cape Sinop and the Kyzil-Irmak River mouth (Fig. 1c). Its basal unit consists of upper Late Euxinic deposits (H_L), practically identical to correlatives in the corresponding horizon on the Kalamitsk shelf. These do not display a sharp lithological break toward overlying Older Black Sea muds, even if these muds are better manifested. The light-gray Late Euxinic carbonate-clay deposits grade upward into a typical "mussel-bearing" mud unit. They include olive-green clayey deposits, rich in *Mytilus* shells with individual coquina layers. Upward in the sequence, the Early Black Sea muds display a sharp lithological break toward Modern deposits. This boundary delineates them with respect to the Kalamitsk shelf deposits.

The 180-cm core at Station 861 (Fig. 1b), Bulgarian shelf, consists entirely of Modern deposits (Late Holocene Unit H_{III}). Lithologically, the deposits are very similar in all three studied areas and consist of uniform, greenish-gray clayey-carbonate and clayey muds (occasionally dark-gray in the upper intervals). They display slight layering with varying amounts of sandy and silty matter; also shell detritus, with whole individual shells.

*A brief lithological sediment characterization, by analytical data, came from the Geology Branch of the expedition. It was compiled under A. V. Komarov, Southern Division, Institute of Oceanology, Russian Academy of Sciences.

The surface unit of the Black Sea shelf deposits is usually underlain by a thin (1-2 cm) yellowish-brown oxidized layer. It often occurs as a ≤ 1 mm thick film or individual brown mottles and smears. This bed is best developed on the Kalamitsk shelf at Stations 797 and 800; the sea bottom area with the "Fe—Mn concretion field" (Fig. 1a). It is represented by local accumulations of *Modiola phaseolina* shells in an oxidized bed, overlain by thin (1-2 mm) ore mineral-overgrowths and crusts, mainly of Fe-hydroxides, with minor amounts of Mn [3]. In sediments of deepest Station 795 (water depth: 150 m) the oxidized film is thin and eroded. Shells are absent here. Minute indications of bottom deposit oxidation were noted also at Stations 822 and 861.

COMPONENT DISTRIBUTION IN HOLOCENE SHELF DEPOSITS

In order to reconstruct the evolving sedimentary process, in reviewing the study results one must observe the sedimentary sequence as it unfolds upward in the section. Changes in the makeup of the studied components within each stratigraphic unit and at lithologic boundaries are of great importance.

Cores at stations on the Kalamitsk shelf (Fig. 1a, Figs. 2a-c; Stations 797, 800, 795) allow comparison between samples from closely adjacent locations on the shelf. They were obtained from significantly different water depths. Similarities and notable differences have both been observed in the component distribution patterns.

Subsurface intervals of the post-Late Euxinic horizon H₁ in all three cores display sediment characteristics that are very similar in terms of composition and alteration trends, involving CaCO₃, organic carbon, Fe-, and S-species. Generally, they have a significant ($\geq 40\%$) carbonate content, more than twice that of corresponding pelagic sediments ($\leq 20\%$). The carbonate ratio is less than in slope deposits (60-70%). On the average, their organic carbon (0.6-0.9%) and total iron content (3-5%) equal that found in post-Late Euxinic deep-water sediments [12]. Both components tend to increase in the unit upward in the section. Increase in the total Fe content is mostly accompanied by increased reactive iron content, an increase related to the iron content in pyrite (Fig. 2b, c). A parallel increase takes place in pyrite-iron and total reactive iron concentrations. Minute quantities of reactive trivalent Fe that occur in Late Euxinic shelf deposits are further reduced in horizons near the Early Black Sea deposits.

Sulfur reduction was almost entirely related to pyrite's sulfur content (maximum 1.2%). Fe-pyrite concentrations increased upward in the section. Other S-species represent minute, admixed contamination: $S_{org} = c. 0.01\%$, $S^0 < 0.01\%$. S^{2-} sulfur in sulfide occurred but in deposits at Station 800, as poorly developed hydrotroilite pigmentation (c. 0.02%).

Transition from Late Euxinic to Early Black Sea units in all cores was accompanied by sharp carbonate content reduction, from 40% to 10-15%. At the same time, the organic carbon content increased slightly. In contrast with deep water deposits, however, the change was very slight and involved mainly increased CaCO₃ content. The maximum change in organic carbon content, c. 1.5%, occurred at Station 797, the shallowest (85 m) of all stations (Fig. 2a).

The conduct of iron and its species at this lithological boundary attracted the most attention. Marked differences occur in total iron, total reactive iron and pyrite-Fe concentrations; both in absolute values and ratios of total reactive iron content in deposits of two adjacent stations (Fig. 2a, b; Stations 797 and 800). The greatest increase in component concentrations was noted in shallowest water Station 797 (83 m depth), while concomitant reduction took place in deepest-water Station 800 of 119 m depth. The total iron concentration was much greater (1-1.5%) than the total reactive iron content (c. 0.5%), indicating that the concentrations of detrital iron forms also varied in the transition zone from Late Euxinic to Early Black Sea deposits. These values increased in shallower and decreased in deeper waters. Additionally, the reactive trivalent Fe practically disappeared at the transition zone. Hydrotroilite disappeared from the core at Station 800, as well (Figs. 2a, b). No significant change was noted in the total iron content at the deepest station (Station 795, water depth: 150 m) near the shelf edge. However, a sharp decline did take place in total reactive- and pyrite-iron content, along with a corresponding increase in detrital iron content (Fig. 2c).

Additional changes in component distribution were observed upward in the section of the Early Black Sea horizon. This was typical in each of the previously cited cores. The carbonate content changed but slightly, with a trend of declining concentrations in shallow-water cores (Stations 797 and 800). Another trend marked a slight carbonate increase in Station 795 (Figs. 2a, b, c), in the homogeneous post-Late Euxinic horizon of reduced thickness. Organic carbon content changes in shallow water cores displayed different trends. The organic carbon content declined in core of Station 797, but increased at Station 800. These changes were typical when the pyrite content remained virtually the same throughout the

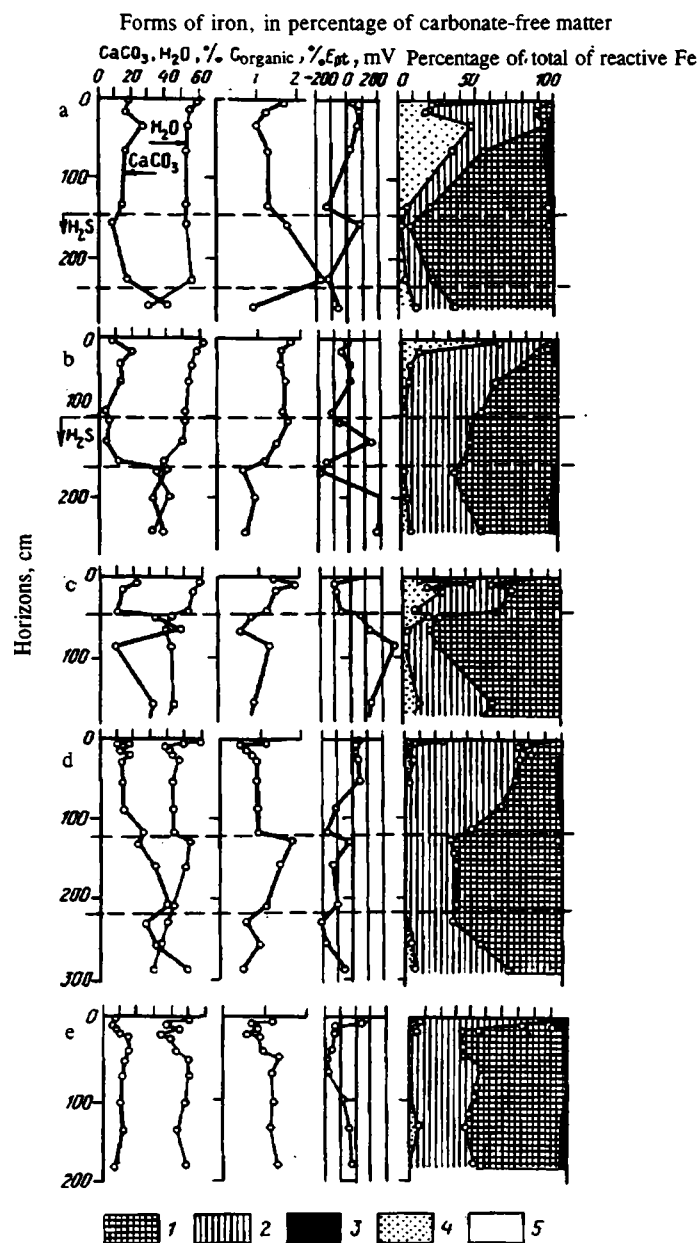


Fig. 2. Component distribution in the deposits: a) Station 797 (83 m); b) Sta. 800 (119 m); c) Sta. 795 (150 m); d) Sta. 822 (99 m); e) Sta. 861 (69 m). Stratigraphic horizons: H_I – Late Novoevksiinsk; H_{II} – Early Black Sea; H_{III} – Late Holocene (modern). Iron forms: 1) Fe in pyrite; 2) sulfide-free Fe(II); 3) Fe in hydrotroilite; 4) reactive Fe(III); 5) detrital forms.

Forms of iron, in percentage of carbonate-free matter

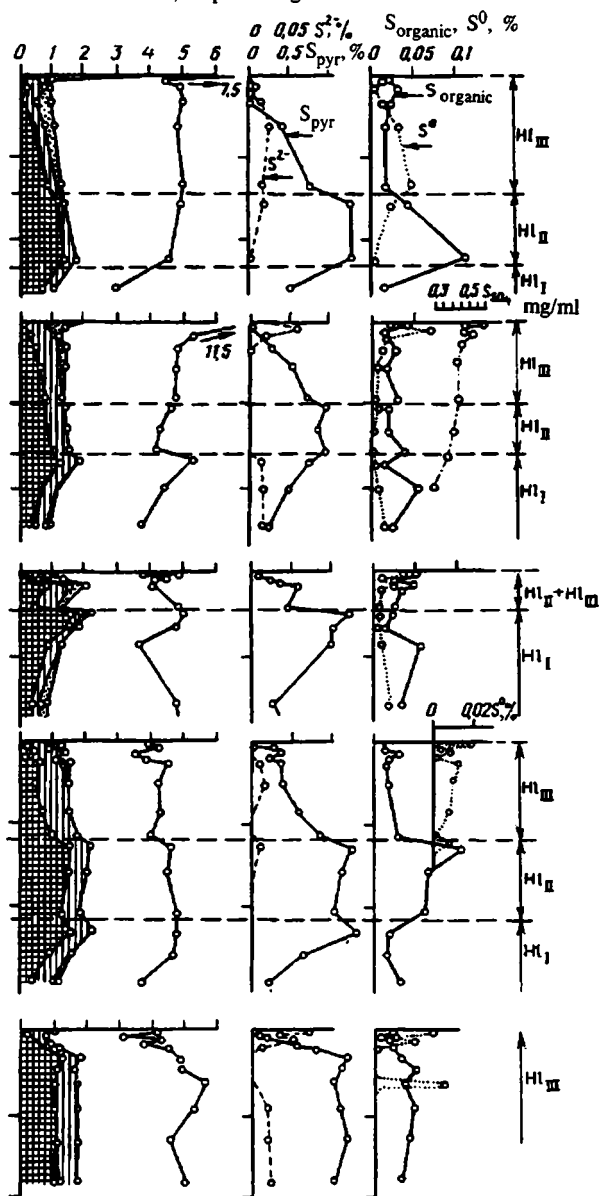


Fig. 2 (continued)

section (S_{pyr} = few percentages of dry sediment weight). Subsequently, the pyrite content diminished gradually with increasing depth. The Fe-pyrite content, as ratio of the total reactive iron content increased in the core at Sta. 797, located in shallower waters. The ratio declined in sediments of deeper water Sta. 800. Due to an increase in the detrital iron-bearing components in both cores, both the total reactive iron and the total iron content increased at the same time. Changes in total iron and total reactive iron concentrations in the Late Euxinic Horizon of Station 795 (Fig. 2c) displayed opposite trends.

The transition from Early Black Sea to modern deposits, very weakly displayed here, was marked by a minor carbonate content increase. Organic carbon, total iron and the total reactive iron concentrations became constant, while the reactive trivalent Fe-content resumed its increase in the hydrotroilite traces of Station 797. In terms of absolute concentrations and total reactive iron content, the pyrite-iron content diminished in a near-linear fashion toward the sediment-water interface (Fig. 2). The upper boundary of the Late Black Sea Horizon approximates the horizon from which free H_2S is absent. This compound occurs in trace amounts in underlying sediments and is identifiable by smell.

Most described component distribution characteristics were also well marked in deposits of the Anatolian shelf (core of Station 822; 99 m depth; Fig. 2c; it greatly resembles core of Station 800, Fig. 2b). The carbonate content did not decrease upward in the section above the lower, erosional boundary of the Early Black Sea Unit but increased by 12-15%. Minor concentration differences account for this fact. At the same time, the total iron content (c.4.5%) remained stable, declining only at the upper unit boundary.

Core 861 on the Bulgarian shelf is composed entirely of Modern deposits. With exception of the c. 40-cm-thick surface unit, it is distinguished by stable component concentration values throughout the section (Fig. 2e).

It is now apparent that, along with well-known overall distribution characteristics of diagenetically active components, Holocene Black Sea shelf sediments are also marked by numerous varied, particular effects due to the distribution pattern. Apparently, these are not accidental features but reflect specific conditions of sediment accumulation and diagenesis during different periods of basin history. They had impacted not only different regions but also various shelf areas. Component distribution patterns in the upper horizons may reflect complex combinations of characteristics that distinguish the surface sediments from underlying deposits. For this reason, each aspect of the associated characteristics should be individually investigated.

COMPONENT DISTRIBUTION IN SURFACE DEPOSITS IN THE OXIDIZED ZONE

In defining distribution characteristics of Fe and S-species that characterize the early diagenetic stage, characteristics of the general features, typical of normally aerated sediments should be studied. Often the FeS_2 content increases in practically linear fashion from traces on the surface or at the boundary of the oxidized interval, to relatively stable, higher concentrations downward in the section. The thickness of the upper horizons with increased FeS_2 -content, varies greatly. In the deepest water Station 795, Kalamitsk shelf (Fig. 2c), this value is c. 20 cm. In sediments of nearby Station 800 (Fig. 2b) the linear FeS_2 increase is restricted to a one-meter interval that corresponds to the entire Modern section. Stabilization of this concentration in the section, as shown by a break in the pyrite sulfur-curve, was associated with the upper boundary of the Early Black Sea horizon. The same pattern emerged from cores of Stations 797 (Fig. 2a) and 822, Anatolian shelf (Fig. 2c). Sediments in core 797 display a slow growth in the FeS_2 content. The increase starts only in the c. 30-cm horizon, above which the pyrite content is small and variable ($S_{\text{pyrite}} \leq 0.1\%$). The upper c. 5 cm of Station 822 sediments is depleted in pyrite. A FeS_2 -increase, starting at the bed boundary, occurs mostly as an abrupt concentration jump from zero to c. 0.30%, rather than as a gradual, slow increase. A sharp, nearly linear increase was noted in the S_{pyrite} curve in core at Station 861, Bulgarian shelf (Fig. 2e). This increase from trace amounts on the surface, to c. 1.15%, occurred within the top 40 cm interval.

Characteristic distribution features of each of the studied components marked the relatively thin (10-20 cm) upper beds of this interval, characterized by increasing pyrite content. This involved in particular in other reduced forms of sulfur (S^{2-} , S^0 , S_{org}), present in much smaller quantities than S in pyrite. In contrast with underlying beds, the surface layer often is significantly enriched in native and sulfide sulfur. The approximately equal concentrations of these species, variable in the thin layers, generally declined downward in the section from 0.06-0.07%, to trace amounts ($\leq 0.001\%$), even to zero (Fig. 2b, Sta. 800; Fig. 2d, Sta. 861). Concentration values correlated well between cores in the vertical sections. Sulfur, present in acid-soluble Fe-sulfides apparently darkened the surface layers. Sulfide-sulfur was absent from

the horizon at Stations 795 and 822 (Fig. 2a, d). The S-content was significantly lower ($\leq 0.02\%$). A typical rhythmic pattern occurred in the S^0 -distribution of the horizon at Station 822 and in its organic carbon content at Station 795. Abrupt variations in the organic S content indicate a somewhat ambiguous correlation with S^{2-} , S^0 ; occasionally also with the organic carbon content. A strong positive correlation between organic S and the organic carbon content is uniformly characteristic of the entire sediment body below these beds (Fig. 2). Minimal sulfate concentrations occur in the muddy pore waters of the 15-20 cm top sediment interval (Fig. 2b, Sta. 800).

As the result of its yellowish-brown oxidized hues, reactive iron in the upper 1-2-cm seafloor sediment layer, at the highest contact levels with bottom waters, often is visually detectable. Iron is mostly in nonsulfide Fe(3) and Fe(2) forms. Trivalent iron occasionally is greatly enriched in this layer (Fig. 2a, b; Stations 797 and 800). No enrichment takes place in other instances. As shown earlier in such relationships, iron found in pyrite is present only in trace amounts in the seafloor layer. Fe-sulfide, as hydrotroilite, may form greater concentrations (maximum 10% of the total reactive iron content; Fig. 2e), or be absent altogether. The total reactive iron content, along with rising FeS_2 concentrations, generally increase downward in the section. Stabilized total pyrite level in this trend coincide exactly with the leveling-off of total reactive Fe-values. Increases in the pyrite-iron content, as ratio of the total reactive iron content usually stop higher than the level at which reactive iron-concentration values become stable (Fig. 2c-e).

In addition to the observed distribution patterns of Fe and S species, surface layer characteristics also include distribution patterns of organic carbon, $CaCO_3$, detrital forms of iron, E_{pt} values and, in numerous instances, the sediment moisture content. Organic carbon values generally increased in these horizons. When this happens, the values occasionally drop to a minimum near the interface between the 1-2-cm top (seafloor) sediment layer and the bottom water layer (Fig. 2d). A slow increase in organic carbon concentration, similar to FeS , may also take place (Fig. 2e). Due to the increased reactive (Fig. 2a, b) and detrital iron content (Fig. 2a, b), the total iron concentration may increase in the subbottom sediment horizon and similarly display rhythmic patterns (Fig. 2c-e). When a sufficient number of analyzed samples are available, the moisture content occasionally also reflects such a pattern (Fig. 2d, e). Significantly, the upper horizon interval often included maximum concentrations of reduced forms of these elements Fe(2), S^{2-} . They correlate with maxima of positive E_{pt} values (Fig. 2d, e).

Some of the cited characteristics may occur individually in buried subbottom sediment horizons. However, virtually all the discussed influences and trends that result from the component distribution patterns, even in the thin (10-20 cm) sea bottom layers of variable thickness occur jointly and distinctly. This close correlation with increasing pyrite content, the main product of sediment diagenesis indicates that these features express specific conditions and variable dynamics that governed the early diagenetic process.

Our data helped to identify the early diagenetic mechanism in seafloor deposits and the depositional and diagenetic conditions that existed during various Holocene intervals.

INTERPRETATION OF RESULTS

Of various factors that control development of reducing forms of Fe and S in the early diagenetic process in the upper sediment beds, the aeration regime, along with the quantity and composition of organic carbon in sediment beds, is the most important aspect. Concentrations of dissolved oxygen in near-bottom and muddy waters, as well as circumstances of their infiltration into the sediments, determined the scale and depth of the oxidation of the dispersed organic matter, distributed in microzones within sediment layers. These are the limiting factors in the process in the development sequence of reactive and microbiologically available oxidized forms that are intermediate between the original organic matter and CO_2 . Such circumstances regulated reducing processes, in particular bacterial sulfate-reduction [4, 9] under subsequent anaerobic conditions.

Evidence for the usual combination of aerobic and anaerobic conditions in the sediments is available not only in the oxidized character of organic compounds (alcohols, aldehydes, ketones, fatty acids), that require sulfate-reducing microorganisms, but also from the fact that the basic S-forms that emerge during diagenesis, are reduced with respect to sulfate ion. At the same time, they represent oxidation products of bacterial hydrogen sulfide or sulfide sulfur of S^{2-} .

Four chemical species of S (S^{2-} , S_{pyrite} , S^0 , S_{org}), formed during diagenesis through interaction between bacterial hydrogen sulfide and organic matter differ from each other in terms of their formation conditions and level of resistance to oxidation by O_2 . Sulfide-S (amorphous and poorly crystallized sulfides of bi- and trivalent iron, H_2S , HS^- , and S^{2-} ,

present in solution and in absorbed state) are very easily oxidized by oxygen even in trace amounts. They form and are preserved only under highly anaerobic conditions. Other species form by direct or indirect oxygen participation, regulated by O_2 -concentration and conditions of interaction.

The formation of S in pyrite involves oxidizing reaction $2S^{2-} - 2e \rightarrow S_2^{2-}$. In addition to O_2 , the oxidizing agent may be trivalent iron, primarily in reactive hydroxide form. In addition to depositional conditions, its accumulation in sediments is also controlled by the aeration regime of the sediments involved:

organic matter O_2

trivalent Fe (enriched) $\rightarrow$ reactive bivalent Fe $\rightarrow$ trivalent reactive Fe.

Native sulfur is the result of even more intensive oxidation of the sulfide form: $S^{2-} - 2e \rightarrow S^0$. all these form under the impact of the same oxidizing agents. Oxidation by O_2 occurs microbiologically or chemically. Unstable intermediate Fe(3)-sulfide compounds may form when S_2^{2-} and trivalent Fe iron interact. Their intraphase precipitation, helped by redox reactions, may be accompanied both by native and pyrite sulfur. In addition, native sulfur may represent the end product of H_2S -oxidation. It may be the oxidizing agent in this pyrite-forming process: $S^{2-} + S^0 \rightarrow S_2^{2-}$.

In comparison with primary S^{2-} , both forms are more stable than hydrogen sulfide. Participation of $O_2(p-p)$ in their formation suggests the possibility that the oxygen concentrations were in semiequilibrium with these forms in the muddy pore waters. As in the "dumbbell" form of sulfur S_n^0 in the most densely packed crystalline pyrite lattice as well as in S- cycles and chains in the system of native S, due to solid bonds and structures under conditions of oxygen deficit their oxidization kinetics may decelerate greatly. Thus S_{pyr} and S^0 form and persist only when the sediments are only moderately aerated. With increased O_2 concentrations, both forms finally become oxidized to sulfate ion. Pyrite oxidization leads exclusively to SO_4^{2-} -formation. Oxidation thus is accompanied by precipitation of a whole sequence of intermediate products (SO_3^{2-} , $S_2O_3^{2-}$, and S_nO_6). They are characteristic participants of biochemical processes. No quantitative evaluation of the oxygen content, pointing to a trend of interactions within this system, is yet available.

Compared with oxygen, dissolved in marine waters, the organic sulfur is highly stable. A strong oxidizing agent, the mix of Br_2 and HNO_3 was used in the extraction from samples. This form apparently does not participate in any further changes in the system. Its presence in the sediments, with exception of the sulfur fraction that initially entered the organic matter, is caused by interaction between organic matter and native sulfur. It may possibly also due to direct oxidation of bacterial hydrogen sulfide by certain groups of organic matter.

Reduction of trivalent iron and sulfate during early diagenetic sediment reorganization proceeds under highly anaerobic conditions. Due to the propensity of Fe^{3+} ion to hydrolyze, in the $Fe(3) \xrightleftharpoons[O_2]{\text{organic matter}} Fe(2)$ -system even small amounts of

free oxygen tend to shift equilibrium to form a Fe(3)-hydroxide phase. Reduction of trivalent Fe may take place both by microbiological and nonbiogenically means, through participation of aerobic and anaerobic hydrolysis-related decomposition products of the organic matter. The organic matter possesses acid and complexing properties. Under these conditions, as during bacterial sulfate-reduction, the role of oxidized organic compounds in the Fe(2) hydroxide phase is of prime importance. The oxidizing character produces the acidity, required in the reduction of the Fe^{3+} ion within the hydroxide group and their neutralization. Even during active reduction of trivalent Fe, in the course of the early diagenetic process the sediment matter undergoes a preliminary aerobic treatment.

Microzonal accumulation may take place under anaerobic conditions due to $O_2(p-p)$ organic matter consumption during oxidation. Trivalent iron reduction occasionally happens prior to sulfate reduction. This fact usually is illustrated by significant differences between normal reducing potential values: $Fe^{3+} \rightarrow Fe^{2+} - +0.771$ V, and $SO_4^{2-} \rightarrow H_2S - +0.303$ V.

However, the predominance of topochemical interrelationships and fermentive katalytic reactions do alter the nature of these processes. Fe^{2+} p-p thus becomes mobile under anaerobic conditions, allowing its migration and combination with nonsulfides; primarily with silicate and Al-silicate phases. Certain portion of these phases apparently may enter carbonates during diagenetic $CaCO_3$ formation or recrystallization. In contrast with Ca^{2+} and Mg^{2+} ions concentrations and due to much lower bivalent Fe^{2+} concentrations in the solution, separate siderite phase does not form. Fe^{2+} only replaces Ca^{2+} and Mg^{2+} in certain lattice positions.

Forms of reactive Fe(2), located in reduced anaerobic microzones, along with unaffected organic reducing agents of the reactive trivalent Fe, during sulfide reduction are influenced by H_2S and corresponding evolving sulfide phases.

Under condition of microzonal evolution of reducing processes in beds that contain oxidizing dissolved oxygen accumulation of reduced Fe and S-forms is inevitably affected by their partial oxidation via diffuse oxygen. In relation to both reagents, the stability of bivalent iron increases in proportion to its association with sulfide-free mineral forms and the level of orderliness in their crystal structures.

The relationship between all discussed processes that involve the diagenetic sulfide formation mechanism have not yet been sufficiently studied. Nevertheless, with exception of S^{2-} the oxidizing character of H_2S -derivatives that accumulate in sediments uniformly points to direct or indirect active participation of dissolved oxygen during development of these forms via the Fe(3) and S^0 -components. Thus, the amount of free $O_2(p-p)$ in the bottom waters or muddy pore waters entirely controls the relationship between aerobic and anaerobic oxidation of organic matter under conditions of its excess, deficit, or absence. It also allows preferential accumulation of certain reduced products of the diagenetic process. Correspondingly, both the general development level of this process and the studied mutual relationships between forms of Fe and S that accumulate in the deposits are related to depositional conditions that control the sediment aeration regime. Therefore, we must briefly describe aeration conditions in the surface sediment layers of the present oxidized marine zone.

Hydrophysical and hydrochemical characteristics of each stratified water layer in the Black Sea have been studied in sufficient detail [17, 21]. The oxidized water horizon represents the aerated surface water layer. Compared with underlying deeper waters, it has the most active and complex hydrodynamic regime. Due to the general counterclockwise circulation, its thickness increases somewhat in nearshore zones (150-180 m) and is reduced in the central region (100-120 m). The boundary between the hydrogen sulfide-bearing and oxygen-rich water layers is marked by O_2 and H_2S -minima (0.05-0.3 mg/liter), by specific reducing-oxidizing, chemical and microbiological processes, as well as certain mixing characteristics of the waters involved. The thickness of this transitional zone varies from 50-70 m in the halistasis centers, to 90 m in areas where in contact with bottom deposits.

Dissolved oxygen distribution is highly variable in the oxygen-enriched water column. The uppermost layers, the top 60-80 m in central areas of the sea and the upper 80-100 m in marginal zones, seasonally are actively mixed. An oxygen maximum, with maximum c. 10 mg/liter O_2 concentrations, develops at 20-30 m depth in the summer. This value corresponds to 130-140% saturation. Oxygen saturation drops to 70-80% by winter's end. Below, oxygen concentrations decline rapidly to 0.5-0.3 mg/liter. This reduction is related to oxygen-loss through consumption, via oxidation processes, and to the declining hydrodynamic energy levels at increasing depths. The lower boundary of the oxidized zone corresponds to a sharp decline in E_p -values in the transition zone, from +450, to -50 mV.

Sediment accumulation in the Black Sea oxidized zone is limited almost exclusively to the shelf area. Shelf depth maxima, 160-180 m, nearly coincide with the oxidized zone's lower limit. Regarding O_2 -distribution in the vertical profile; extensive bottom areas, primarily those below the convective mixing layer (80-100 m), suffer of constant oxygen deficit. One must also consider the heterogeneous conditions and the hydrodynamic mobility of the transitional zone. The most powerful zone of counterclockwise current flow regularly extends beyond the outer shelf limits [22, 23]. This results in the periodic impact on bottom sediments by oxygen-depleted waters in the transitional zone; probably occasionally also by hydrogen sulfide-enriched waters. Due to the general oxygen deficit in bottom waters, over a large portion of the Black Sea shelf, in various areas the intensity of sediment aeration changes with depth and time.

In addition to conditions that supply the seafloor with oxygen (increased bioproductivity, closeness, and characteristics of hydrology of hydrogen sulfide-bearing water), one must consider factors that facilitate aeration of sediments. Due mainly to wave action that greatly mobilizes sediment matter, sediment accumulation on the shelf is influenced by unusually high hydrodynamic levels. Constancy in the shelf sediment accumulation regime under these conditions results in relatively permanent values in dynamic factors that include speed and direction of nearshore currents, current gyres, their thickness and frequency, pulses of the major littoral currents, as well as the quantity and composition of sediment matter that reaches the sea bottom within given time intervals. The relationship between these factors in each shelf area determines the nature of sediment reworking and the granulometric and density differences; in general the intensity and selectivity of transport of biogenic and terrigenous matter toward slope and the deep basin areas.

Sediment across the shelf is transported mostly by periodic violent currents that occasionally redistribute and rework seafloor beds of variable thicknesses. Thickness depends on the scale and speed of the bottom currents. In the middle shelf zone these beds probably are few tenths of one meter thick. They generally thin with increasing water depth [1, 2]. The rate of sediment redistribution may vary considerably. Thicker and thinner horizons of homogenous mud horizons may form on the shelf as the result. Thus, the diagenetic processes in shelf floor deposits are not only uneven, associated by insufficient aeration of the bottom sediments, but also involve intensive sediment reworking. Due to the

oxygen-rich bottom waters during sediment reworking, greatly increased oxidation of the organic sedimentary matter and diagenetically formed Fe and S-compounds takes place. Transport of these compounds toward deep basin area; fractionation by grain size, density, hydrodynamic and surface characteristics of the dispersed particles, as well as aggregates that contain these chemical forms occurs under anaerobic conditions.

Increased oxidation of reduced chemical forms also leads to mixing of sediments from the top (seafloor) sediment horizons by benthic organisms. The thickness of the layer, accessible to consumption by detritus-feeding organisms in the nearshore zone was calculated as several tens of cm [28]. Bioturbation actively affects sediment reworking, but its role in the process is yet unclear. Loosening of sediments leads to reworking of the upper, seafloor horizon; also to enhanced oxygen diffusion. To some extent, this apparently is compensated by the formation and size increase of organic-mineral particles through surface-active benthic secretions. Such processes also favor sediment fractionation.

* * *

Changes in the aeration regime of surface sediment layers in sediment accumulation throughout geological time indicate the influence of diagenesis on the distribution characteristics in sediment beds and changes in the quantity and composition of the organic matter that enters them. All of these changes are closely interrelated and generally dependent on the bioproductivity of a given area. They are to be taken into account when interpreting data obtained from all the studied Holocene sedimentary units. In examining specifics of the early diagenetic process in various periods of Late Quaternary geochemical history of the basin, one must consider that a significant part of the present Black Sea shelf was involved in marine sediment accumulation during the last, postglacial transgression. For this reason, conditions of aeration, re-deposition and fractionation of the sediment matter; their relationship to the evolving bioproductivity processes and the dynamics of hydrogen sulfide zone evolution gradually changed in each region of the shelf. These factors were also associated with water depth increases.

Assumptions on the specific role of the aeration regime in surface deposits during development of the early diagenetic process were utilized in sediment studies in the Morocco Basin [13], the Caspian Sea [14], the Bay of Bengal [15] and the hydrogen sulfide-enriched zone of the Black Sea [12]. The investigations were based, on one hand on a number of microbiological studies [4, 9], on the other, they dealt thoroughly with redox conditions in the Fe-S system and chemistry of diagenetic alteration products of these elements [16]. Such an approach to marine sediments explains many distribution patterns of Fe and S-species very well and was easily adapted to the Black Sea shelf. It illustrates the relationship between features of the early diagenetic process, its effects under physical and biochemical field conditions of sediment accumulation and during changes that touch on basin evolution. Investigation results (Fig. 2) that relate to these issues are the subject of the next paper.

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GEOCHEMISTRY OF RARE EARTH ELEMENTS IN THE FORMATION OF FERROMANGANESE NODULES IN THE PERUVIAN TROUGH OF THE PACIFIC OCEAN

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The behavior of Fe, Mn, Al, P, Co, Ni, Cu, and the rare-earth elements in myopelagic deposits and nodules, as well as in the upper and lower parts of nodules from the same bottom-dredged sample taken in the Peruvian Trough of the Pacific Ocean is considered. It is shown that iron and phosphorus enrich the lower parts of nodules, and manganese the upper parts, and that this is due to the greater mobility of manganese in processes of reducing diagenesis in sediment. The content of copper and nickel in the nodules correlates directly with that of manganese, while that of cobalt and the rare-earth elements, with iron. Analysis of the contents of the reactive portion of the rare-earth elements in the nodules and in the sediment they are found in as measured in a Chester extract demonstrated that the composition of the rare-earth elements in the nodules could have been obtained from the reactive part of the sediment. The difference in the compositions of rare-earth elements in the nodules and sediment is determined by the differing degrees of mobility of the ferrihydroxides and iron phosphates in processes of diagenetic redistribution in sediment in the course of the formation of nodules.

Investigation of processes of ore formation in the ocean ultimately entails answering two essential questions. First, what could be the sources of matter and, second, what could be the mechanism of processes that are responsible for the formation of the composition of ferromanganese nodules. It is quite clear how the first question should be answered, and most investigators now believe that oceanic water as well as the surrounding sediment (including interstitial water) are the sources of the matter in the nodules.

The second question is more complicated, since the importance of the processes that lead to the formation of nodules varies as a function of the reduction-oxidation conditions in the sediment, the rates of sedimentation in the particular region, the composition of the sedimentary material, as well as, possibly, the topography, depth of occurrence of the nodules, and so on [1, 11, 12, 15].

In most cases a compound sedimentary-diagenetic mechanism is believed to be responsible for the formation of a nodule, moreover a sedimentary process by which matter is transported is assumed to be typical of the iron group (rare-earth elements, cobalt, thorium), while a diagenetic process is assumed to be characteristic of the manganese group (copper, nickel, zinc). Differences in the composition of the upper and lower parts of nodules [11, 18] attest to the role of early diagenesis in the sediments in the delivery of matter for construction of the nodules. In addition, the lowermost strata of the nodules are usually enriched with manganese, copper, nickel, molybdenum, and zinc, and the uppermost strata, with iron, cobalt, and lead. Calvert and Price [12] attributed this difference to delivery of metals associated with manganese oxyhydroxides from the subjacent sediment, as well as direct delivery of metals associated with ferrihydroxides from the seawater into the upper parts of the nodules. Intensive processes of diagenesis in the surrounding sediment is responsible for the dominant growth of the lower part of the nodules, a circumstance that leads to asymmetry of the nodules [17]. Thus, the Mn/Fe ratio may, to some degree, attest to the presence of two mechanisms in the creation of nodules. It is because of the dominance of the sedimentary mechanism (sedimentation from seawater) that the value of the Mn/Fe ratio is close to unity.

Until now scientists have rarely referred to the rare-earth elements in trying to determine the genesis of nodules in assemblages with surrounding sediment. As regards the iron group, lanthanoids in the nodules may give us information concerning the genesis of ferrihydroxides. In their investigation of the composition of the rare-earth elements in nodules Goldberg et al. [23] and Piper [27] were led to conclude that the rare-earth elements were extracted from the oceanic

water by the ferric hydroxide. Hydrogeneous ferrihydroxides in pelagic nodules and crust with a rare-earth composition may be the basic factor responsible for changes in the composition of dissolved rare-earth elements in oceanic pelagic zones [3]. The basic features of this composition is the positive cerium anomaly and the maximal build-up of intermediate rare-earth elements (cf. [22, 28]).

Though it is evident from the available data that the composition of the nodules is far from fixed and, in addition to the positive cerium anomaly, a cerium deficit and the dominance not of intermediate but of the heavy rare-earth elements, have also been discovered in the nodules, these nodules are often found in sediment with similar rare-earth composition in zones affected by hydrothermal factors [14, 22]. In this case the content of the rare-earth elements in the nodules does not exceed their content in the sediment, and the sediments appear to be the preferred source of matter for the nodules.

The Peruvian Trough of the Pacific Ocean is among of the regions in which there is a distinctive negative cerium anomaly in the rare-earth sediments and where the heavy lanthanoids dominate the light and intermediate forms, moreover where the negative cerium anomaly is not inherited by the nodules [14, 22]. The purpose of the present article is to explain the causes and mechanisms underlying the processes responsible for the difference in the composition of rare-earth elements in the nodules as compared with the surrounding sediment.

MATERIAL AND METHODS OF ANALYSIS

Material for the study was obtained on the 26th voyage of the *Akademik Korolev* research vessel in 1980 [6]. Bottom-dredged nodules and sediment that are the subject of the present study were taken at column 56 (13°15'S, 86°00' W, depth 4600 m). The sediment from the site (0-10 cm) were represented by myopelagic clay with a large quantity of nodules at the 0-6-cm horizon. Six nodules that differed in terms of morphology were selected for investigation. The position of the nodules in the bottom dredge relative to the surface of the floor was labeled prior to extraction from the sediment.

Sample 56/1, a multicore cluster-shaped nodule with at least four cores; 3 × 4 cm in dimension.

Sample 56/2, an angular nodule probably with the shape of a core; surface is slightly bumpy; 3.5 × 5 cm in dimension.

Sample 56/3, elongated, ellipsoidal nodule with long axis situated in the vertical direction; 2 × 5 cm in dimension.

Sample 56/4, ellipsoidal nodule, with long axis in the horizontal direction; the upper and lower surfaces are morphologically distinct, with the upper surface bumpy and the lower surface smoother with traces of sediment submer-sion; 4.5 × 7 cm in dimension.

Sample 56/5, morphologically analogous to nodule 56/4; 5 × 7 cm in dimension.

Sample 56/6, disk-shaped nodule with bumpy upper surface and smoother lower surface with traces of sediment; 4.5 × 7 cm in dimension.

Bulk samples were taken from Samples 56/1 and 56/2. The upper and lower surfaces (down to 10 mm) were selected in the case of nodules 56/3 - 56/6. The position of the nodule in the sediment when it was lifted in the dredger as well as morphological characteristics were used as a basis for determining the upper and lower surfaces. The lower surfaces were smoother with traces of argillaceous sediment, while the upper surfaces were "bumpier". without any traces of sediment. Nodule 56/3 did not exhibit any distinctive features in terms of surface morphology, and the selection of the upper and lower parts of the nodule was based exclusively on the position of the nodule in the sediment that was present in the dredger.

Pulverized air-dried samples were analyzed by mass spectrometry with an inductively coupled plasma on the Plasma Quad PQ2 + Turbo device produced by the firm of VG Instruments. The method employed two internal standards (In - Re) and followed a technique described in detail in [4]. The results of the analysis were tested against the standard samples AGV-1 and GSP-1. The data obtained for the standard samples, as well as data for the isotopes that were used as a basis for the calculations, are presented in Table 1. The reproducibility of the analysis for all the lanthanoids was above 10%.

TABLE 1. Isotopes Used in Analysis of Rare-Earth Elements and Content of Rare-Earth Elements in the Standard Samples AGV-1 and GSP-1

Element	Isotope	AGV-1 (andesite)		GSP-1 (granodiorite)	
		1	2	1	2
La	¹³⁹ La	40,1	38	195	184
Ce	¹⁴⁰ Ce	70,5	67	449	399
Pr	¹⁴¹ Pr	8,73	7,6	57,9	52
Nd	¹⁴⁵ Nd	33,1	33	214	196
Sm	¹⁴⁷ Sm	6,31	5,9	27,2	26,3
Eu	¹⁵¹ Eu	1,59	1,64	2,19	2,33
Gd	¹⁶⁰ Gd	5,18	5,09	12,5	12,1
Tb	¹⁵⁹ Tb	0,67	0,70	1,29	1,34
Dy	¹⁶³ Dy	3,84	3,60	6,02	5,5
Ho	¹⁶⁵ Ho	0,75	0,67	0,91	1,01
Er	¹⁶⁶ Er, ¹⁶⁷ Er	2,01	1,70	2,27	2,7
Tm	¹⁶⁹ Tm	0,25	0,34	0,24	0,38
Yb	¹⁷² Yb, ¹⁷³ Yb	1,61	1,72	1,21	1,7
Lu	¹⁷⁵ Lu	0,24	0,27	0,15	0,214

Remark. Data obtained in the present study are listed in column 1, and previously collected data in column 2.

Determination of iron, manganese, aluminum, copper, cobalt, and nickel was conducted by N. N. Zavadskaya by means of atomic absorption spectrometry in a plasma variant using a Perkin Elmer 403. The reproducibility of the analysis was at least 3 rel.%. Phosphorous was determined by means of the molybdenate method [7] completed either using the titrimetric or the spectrophotometric technique.

DISTRIBUTION OF RARE-EARTH ELEMENTS IN BULK SAMPLES OF SEDIMENT AND NODULES

Data on rare-earth elements, iron, manganese, aluminum, and phosphorus in sediment from four horizons at the site are presented in Table 2. Despite the fact that the sediment from the column represent, according to the Bostrom criterion ($Al/Al + Fe + Mn > 0.4$) [10], nonhydrothermal varieties, the composition of the rare-earth elements in this sediment exhibits features that are characteristic of dissolved rare-earth elements from seawater (Fig. 1). A negative cerium anomaly and deficit of light rare-earth elements can be clearly observed. One of the present authors has previously succeeded in demonstrating for the case of the sublatitudinal profile of sediment across the 17°S parallel of the Eastern Pacific Uplift that the variation in the composition of rare-earth elements towards increasing Ce anomaly and increasing rate of build-up of light rare-earth elements is quite constant and is determined by the decrease in the proportion of ferrihydroxides of hydrothermal origin [5]. This process has more recently been demonstrated for compositions of rare-earth elements in a suspension of hydrothermal iron that had been extracted from thermal springs [20].

The content of iron, manganese, aluminum, copper, nickel, cobalt, phosphorous, and the rare-earth elements in the bulk samples of nodules 56/1 and 56/2 and in the upper and lower parts of nodules 56/3-56/6 are presented in Table 3. It is clear from this table that the content of iron and manganese in the nodules collected in a single bottom dredge varies rather significantly, in the ranges 8.2-13.6% and 20.2-27.6%, respectively. The upper parts of the nodules are enriched with manganese, and the lower parts with iron. The distribution of iron and manganese in the upper and lower parts of the nodules is opposite to that found in [18] for three nodules from the Clarion Clipperton region. The differences in the content of iron and manganese between the lower and upper surfaces are greatest in the case of nodule 56/4, amounting to 4% for iron and 2.4% for manganese; in the other nodules the differences in the content of iron and manganese does not exceed 1%, while in nodule 56/6 there are no differences between the upper and lower surfaces. Thus, the differences in the chemistry of the composition of the nodules (iron and manganese) within a single bottom dredge is greater than the difference between the upper and lower surfaces of the nodules. The bulk content of aluminum is higher in the upper parts of the nodules in the case of three of the four nodules.

TABLE 2. Content of Elements in Bulk Samples of Sediment from Column 56 and in Shale (NASC)

Element*	Horizon, cm				Shale
	0—1	1—3	3—6	6—10	
La	43,5	42,1	44,8	49,9	32
Ce	57,0	53,9	56,7	62,9	73
Pr	10,8	10,0	11,0	11,9	7,9
Nd	43,4	44,3	43,2	50,0	33
Sm	11,0	11,1	11,0	13,0	5,7
Eu	2,66	2,75	2,75	2,84	1,24
Gd	10,9	10,8	11,7	12,4	5,2
Tb	1,83	1,56	1,59	1,82	0,85
Dy	10,2	10,1	11,1	12,7	5,2
Ho	2,21	2,29	2,39	2,69	1,04
Er	7,11	6,44	7,34	8,08	3,4
Tm	1,02	1,03	1,16	1,25	0,5
Yb	6,46	6,91	6,99	7,47	3,1
Lu	1,09	1,01	1,07	1,11	0,48
Fe	4,37	4,05	4,43	4,48	—
Mn	0,77	0,70	0,52	0,36	—
Al	6,16	5,87	6,34	6,31	—
P	0,19	0,22	0,19	0,20	—

*The contents of iron, manganese, aluminum, and fluorine are given as percentages, while the contents of the other elements are given in terms of g/ton.

According to the Bonatti [9] classification, the content of copper, cobalt, and nickel corresponds to the analogous content in the case of hydrogeneous ferromanganese deposits in the ocean. The content of copper and nickel correlate with the content of manganese, while the cobalt content recalls the behavior of iron (Table 4).

The content of the rare-earth elements is higher in the nodules than in the sediment and, as is also true of cobalt, correlates directly with the iron content (cf. Table 4). The compositions of rare-earth elements in the nodules exhibits a weak positive cerium anomaly and differs from that of the sediment by virtue of a build-up of light rare-earth elements (Fig. 2). In every case the upper less ferruginous parts of the nodules exhibit a less positive cerium anomaly, judging from the Ce/Nd ratio and in lesser build-up of light rare-earth elements. The values of the Nd/Er ratio in the upper parts of nodules 56/4 and 56/5 (which differ significantly with respect to iron content between the upper and lower parts of the nodules) are less than in the lower parts of the nodules. This indicates that the increase in the positive cerium anomaly on the lower surfaces of the nodules is a consequence of the build-up of cerium itself against a background of a preferred build-up of light as opposed to heavy rare-earth elements. Phosphorous in the nodules is, apparently, also associated mainly with the iron content. Consequently, it does not form a separate phase (apatite), but instead occurs in a sorbed complex of ferrihydroxides.

FORMS OF RARE-EARTH ELEMENTS IN SEDIMENT AND NODULES

Investigation of bulk contents in nodules demonstrated that the composition of rare-earth elements in these nodules differs from that observed in sediment, whereas the content of individual rare-earth elements (including cerium) depends strongly on the content of iron, the maximal value of which is confined to the lower surface of the nodules that had been formed in the sediment. The cause for enrichment of the lower parts of the nodules with iron and rare-earth elements must apparently be sought in the composition of rare-earth elements from column 56. The myopelagic clays with a small (up to 20%) CaCO_3 impurity from column 56 were thoroughly investigated in [6]. Investigation of the macro-composition of the sedimentary core (270 cm) presented in [6] demonstrated that the sediment from column 56 was affected by processes of early reducing diagenesis, in that manganese content is not constant but rather varies throughout the column from 0.07%

TABLE 3. Content of Elements in Nodules from Column 56

Element*	56/1	56/2	56/3		56/4		56/5		56/6	
			upper surface	lower surface	upper surface	lower surface	upper surface	lower surface	upper surface	lower surface
La	119	164	120	128	96,2	138	96,8	104	114	119
Ce	297	441	308	330	242	375	261	289	290	297
Pr	27,1	33,6	27,6	29,6	21,9	31,7	23,1	25,3	27,4	27,8
Nd	113	138	117	121	93,9	132	94,3	104	113	116
Sm	25,5	30,3	25,8	26,8	23,1	32,7	23,3	26,6	24,4	23,7
Eu	6,03	7,18	5,90	6,12	5,41	7,82	5,43	6,26	5,63	5,51
Gd	26,9	31,9	26,3	27,2	22,8	33,4	22,3	23,7	24,9	25,5
Tb	4,16	4,81	4,09	4,16	3,77	4,87	3,40	3,60	3,79	3,89
Dy	27,3	32,3	25,7	26,2	23,4	29,6	22,4	23,3	25,6	24,7
Ho	5,80	6,84	5,14	5,23	4,77	6,18	4,29	4,80	5,29	5,14
Er	16,6	20,0	14,5	14,9	13,6	17,9	13,6	13,9	15,0	15,3
Tm	2,40	2,98	2,16	2,06	2,17	2,67	1,94	2,17	2,34	2,22
Yb	15,9	20,0	13,4	14,8	13,6	18,2	12,5	12,6	14,1	14,5
Lu	2,53	3,02	2,07	2,22	1,87	2,50	1,80	2,04	2,27	2,14
Cu	0,43	0,36	0,55	0,55	0,64	0,44	0,62	0,58	0,66	0,52
Ni	1,08	0,92	1,24	1,20	1,30	1,03	1,21	1,31	1,24	1,27
Co	0,14	0,18	0,15	0,16	0,10	0,15	0,09	0,11	0,15	0,15
Fe	10,8	13,6	10,7	11,2	8,60	12,6	8,21	9,26	9,74	9,77
Mn	20,2	22,1	23,4	22,5	26,2	23,8	27,6	26,2	25,9	25,2
Al	2,83	1,51	1,89	2,06	2,31	1,45	2,20	2,15	1,78	1,53
P	0,26	0,26	0,19	0,23	0,21	0,30	0,21	0,20	0,21	0,21

*The contents of copper, nickel, cobalt, iron, manganese, aluminum, and fluorine are given as percentages, while the contents of the other elements are given in terms of g/ton.

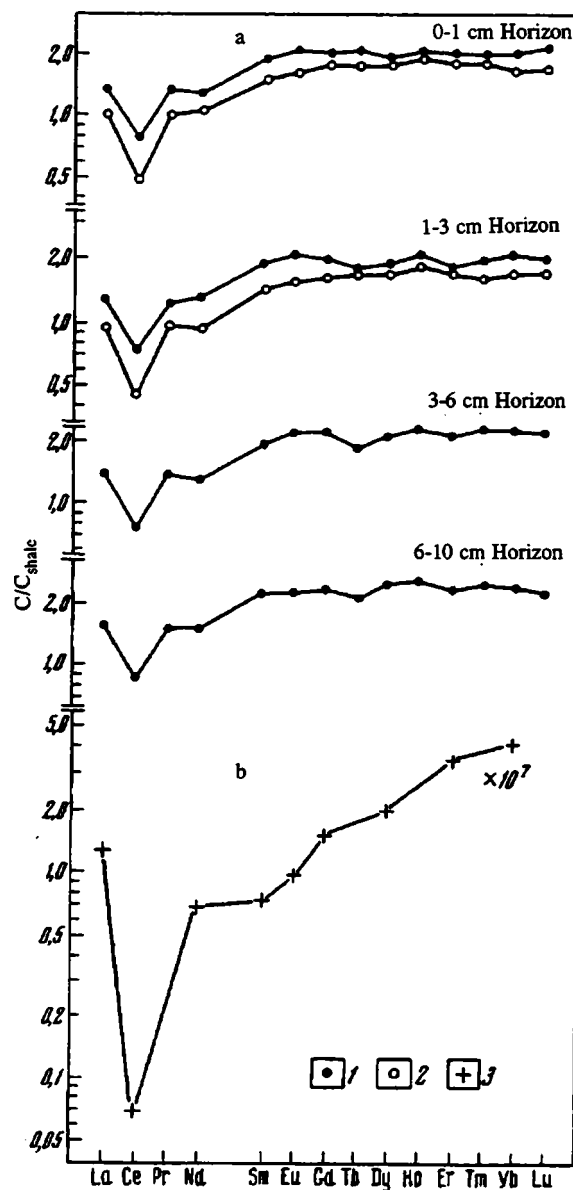


Fig. 1. Compositions of rare-earth elements in sediment from column 56 (a) and dissolved rare-earth elements of internal water of the ocean (b) [25]: (1) bulk sample of sediment; (2) Chester extract; (3) oceanic water.

to 1.38%. Of the five samples of sediment taken from the bottom dredge (two samples from the 0-1-cm horizon were studied), the maximal (26% of the bulk content) relative content of reactive iron was discovered in the 3-6-cm layer as opposed to 20-22% in the 0-1-cm layer.

The formation of the sediment is associated with a build-up of matter on the ocean floor from a number of likely sources, including hydrothermal, hydro-, bio-, litho-, and edaphic sources. Since the material found in the ferromanganese nodules is represented primarily by ferric and manganese oxyhydroxides, we were interested mainly in the composition of ferric and manganese oxyhydroxides in the sediment. For this reason the sediment found in 0-1-cm and 1-3-cm horizons (about 50 mg) were subjected to a low-temperature treatment in a 1 M solution of $\text{NH}_2\text{OH} \cdot \text{HCl} + 25\% \text{CH}_3\text{COOH}$ (20 ml) for 4 h using a technique described in [13]. This extract, which was proposed by R. Chester and M. Hughes, produces a yield of up to 100% of the weakly crystallized manganese oxyhydroxides and up to 90% of the weakly crystallized ferrihydroxides, entailing, moreover, only an insignificant consumption of the aluminosilicate (including authigenic), and

TABLE 4. Correlation Coefficients between Elements in Bulk Samples of Nodules from Column 56 (n = 10, r = 0.632 with P = 0.95)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
La	1,000	0,980	0,965	0,964	0,790	0,769	0,906	0,905	0,961
Ce		1,000	0,949	0,938	0,860	0,843	0,908	0,887	0,938
Pr			1,000	0,994	0,823	0,791	0,921	0,885	0,915
Nd				1,000	0,818	0,786	0,934	0,912	0,926
Sm					1,000	0,995	0,928	0,879	0,818
Eu						1,000	0,919	0,870	0,813
Gd							1,000	0,981	0,937
Tb								1,000	0,949
Dy									1,000
	Ho	Er	Tm	Yb	Lu	Al	Fe	Mn	P
La	0,934	0,934	0,851	0,921	0,923	-0,555	0,972	-0,668	0,644
Ce	0,902	0,921	0,853	0,905	0,889	-0,595	0,957	-0,567	0,661
Pr	0,887	0,876	0,778	0,856	0,869	-0,618	0,955	-0,637	0,634
Nd	0,902	0,878	0,791	0,865	0,867	-0,617	0,965	-0,665	0,633
Sm	0,787	0,785	0,756	0,801	0,712	-0,504	0,873	-0,465	0,800
Eu	0,792	0,798	0,779	0,813	0,718	-0,471	0,853	-0,451	0,830
Gd	0,913	0,903	0,834	0,922	0,837	-0,535	0,962	-0,638	0,841
Tb	0,930	0,900	0,846	0,936	0,842	-0,473	0,964	-0,695	0,819
Dy	0,987	0,972	0,921	0,971	0,959	-0,437	0,974	-0,715	0,771
Ho	1,000	0,976	0,951	0,969	0,975	-0,402	0,948	-0,722	0,760
Er		1,000	0,950	0,982	0,966	-0,438	0,923	-0,646	0,789
Tm			1,000	0,936	0,922	-0,463	0,846	-0,507	0,715
Yb				1,000	0,934	-0,439	0,924	-0,636	0,841
Lu					1,000	-0,326	0,907	-0,728	0,701
Al						1,000	-0,475	-0,148	-0,185
Fe							1,000	-0,738	0,736
Mn								1,000	-0,541
P									1,000
	Cu	Ni	Co						
La	-0,842	-0,854	0,880						
Ce	-0,821	-0,856	0,796						
Pr	-0,780	-0,775	0,914						
Nd	-0,791	-0,769	0,927						
Sm	-0,721	-0,756	0,563						
Eu	-0,737	-0,770	0,515						
Gd	-0,830	-0,852	0,757						
Tb	-0,836	-0,846	0,763						
Dy	-0,858	-0,923	0,815						
Ho	-0,867	-0,893	0,802						
Er	-0,898	-0,942	0,739						
Tm	-0,784	-0,851	0,648						
Yb	-0,866	-0,931	0,718						
Lu	-0,857	-0,895	0,796						
Al	-0,224	-0,259	-0,534						
Fe	-0,860	-0,865	0,848						
Mn	0,777	0,650	-0,694						
P	-0,732	-0,847	0,393						
Cu	1,000	0,868	-0,639						
Ni		1,000	-0,594						
Co			1,000						

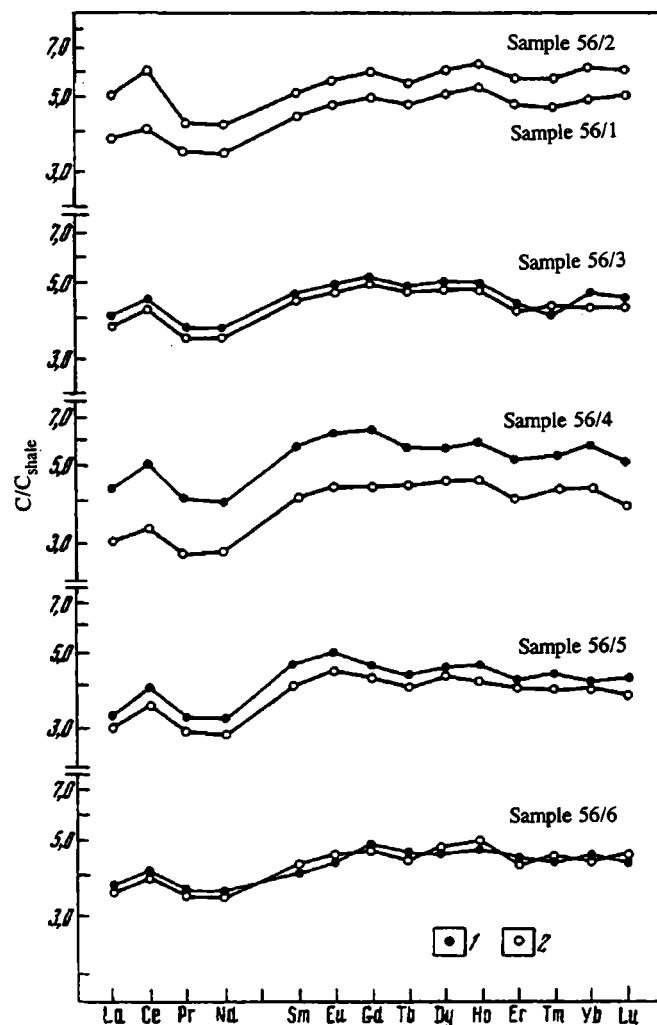


Fig. 2. Composition of the rare-earth elements in bulk samples of nodules from column 56. 1 and 2 refer correspondingly to the lower and upper parts of the nodules.

also, according to our data, without any consumption of the apatite and barite, minerals in which rather significant build-up of rare-earth elements is possible [19, 24]. However, treatment with this reagent, besides dissolving the ferric and manganese oxyhydroxides, will also dissolve calcium carbonate and yield a sorbed assemblage of minor elements of the other constituents of the sediment. The content of the rare-earth elements in the skeleton of the foraminifer, which is the principal source of CaCO_3 in sediment from column 56, is extremely low [26]. Moreover, together with the minor elements of ferric and manganese oxyhydroxides, it is possible for the minor elements of the sorbed assemblage to occur entirely in the composition of the nodules.

Though, judging from the aluminum content, the nodules from column 56 exhibit insignificant quantities of nonmetalliferous matter, these nodules (that is, those from columns 56/4-56/6) were also subjected to treatment with Chester reagent using a technique analogous to that employed with the sediment. The content of iron, manganese, aluminum, phosphorous, and the rare-earth elements in the extracts taken from the sediment and nodules are presented in Table 5.

Comparison of the data in Tables 2 and 5 shows that roughly 15% of the iron (of the bulk content), nearly all the manganese, about one-half of the phosphorus, and only around 8% of the total content of aluminum is extracted from the sediment by means of the Chester reagent. Moreover the yield of the rare-earth elements from the sediment amounts to

TABLE 5. Content of Elements in Extracts from Sediment and Nodules from Column 56

Element *	Sediment		Nodule					
	Horizon, cm		56/4		56/5		56/6	
	0—1	1—3	upper surface	lower surface	upper surface	lower surface	upper surface	lower surface
La	32,0	30,5	93,0	139	91,9	98,0	113	119
Ce	35,3	32,7	240	373	244	266	283	297
Pr	8,05	7,77	22,0	31,6	21,2	23,3	26,3	26,8
Nd	35,7	30,8	91,0	127	90,0	95,6	107	110
Sm	8,81	8,42	22,2	32,6	22,2	23,0	24,2	24,5
Eu	2,02	2,00	5,24	7,18	5,17	5,42	5,71	5,87
Gd	9,57	8,80	22,2	32,1	23,4	24,4	25,5	25,5
Tb	1,53	1,49	3,25	4,86	3,40	3,66	4,00	3,86
Dy	9,62	8,97	20,9	29,6	20,0	21,9	25,5	25,0
Ho	2,09	1,99	4,58	6,38	4,17	4,68	5,21	5,17
Er	6,31	6,05	12,8	17,7	12,5	13,4	15,2	14,7
Tm	0,95	0,83	1,96	2,88	1,97	2,20	2,20	2,10
Yb	5,33	5,59	12,9	17,8	12,6	12,9	14,1	13,6
Lu	0,84	0,86	2,10	2,50	1,71	1,90	2,30	2,19
Al	0,47	0,47	0,98	0,70	1,08	1,18	1,20	0,80
Fe	0,66	0,59	7,38	11,3	6,83	7,53	8,21	8,30
Mn	0,68	0,67	25,4	23,5	27,6	25,6	25,9	25,5
P	0,13	0,10	0,178	0,238	0,159	0,159	0,159	0,189

*The contents of aluminum, iron, manganese, and fluorine are given as percentages, while the content of the other elements are given in terms of g/ton.

60-95%, with cerium and the light rare-earth elements the least likely to be present in the extract. The compositions of rare-earth elements in the extracts from the sediment exhibit (relative to the bulk samples) a higher deficit of cerium and the light rare-earth elements (cf. Fig. 1), i.e., the composition of the hydroxide constituents of the sediment becomes greater, and comes to resemble the composition of dissolved rare-earth elements in oceanic water, which supports the hypothesis that iron of hydrothermal origin participates in the sedimentation process [5].

Extraction of iron from the nodules of column 56/4-56/6 varies in the range from 81% to 89% (as percentages of the bulk contents); nearly 100% of the manganese is extracted; only 43-68% of the aluminum and 74-92% of the phosphorus are extracted, while the laws that usually govern extraction of minor elements from the upper and lower parts of the nodules were not observed. Nearly 100% of the rare-earth elements were extracted from the nodule samples without any change in the features of these compositions, which are also typical of the bulk samples (Fig. 3).

DISCUSSION

Investigations of the bulk contents of elements in the nodules and of the content of rare-earth elements are associated in these nodules with the iron content (cf. Table 4), which is characteristic also of the Chester extracts from nodules (Fig. 4). In this case we also observe a direct dependence of the content of rare-earth elements on the iron content, moreover the approximation of a linear dependence on iron content in the range 0.59-0.66% (as in the Chester extracts from the sediment) corresponds to content of the lanthanoids in the Chester extracts from the sediment. Consequently, the observed compositions of rare-earth elements in the nodules could have resulted from the reactive portion of the sediment, basically from the ferric and manganese oxyhydroxides without making any assumptions as to any additional source of matter.

The build-up of reactive iron in the nodules is accompanied by varying degrees of build-up of lanthanoids. The mean values of the build-up factor for the elements in the nodules relative to the reactive portion of the sediment are as follows:

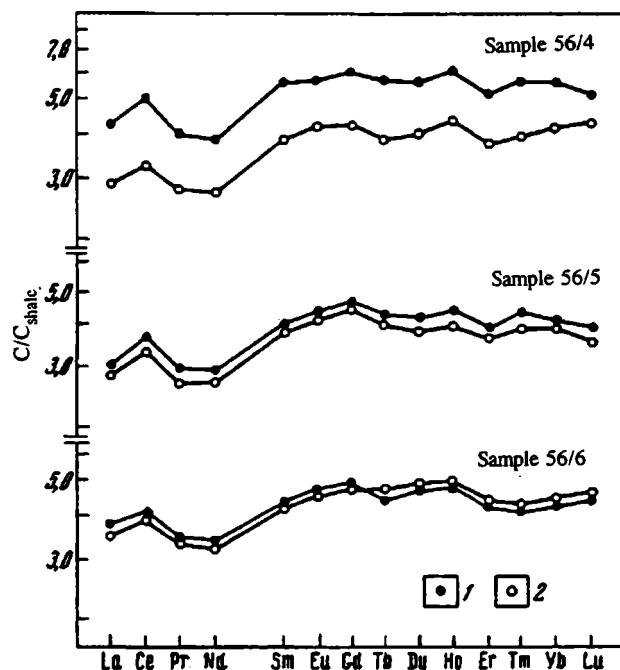


Fig. 3. Compositions of rare-earth elements in extracts from nodules of column 56. 1 and 2 refer, correspondingly, to the lower and upper parts of the nodules.

$Mn > Fe > Ce > La > Pr > Nd > Sm = Eu > Cd > Tb...Ho = Tm...Lu > Er$
 37,9 13,2 8,4 3,5 3,2 3,1 2,9 2,8 2,6—2,5 2,3
 $> Al > P$
 2,1 1,6

Of all the lanthanoids, cerium exhibits the greatest build-up (by a factor of 6.8-10.6), and after cerium there follow, in terms of degree of enrichment, the light rare-earth elements, then the intermediate rare-earth elements, and finally the heavy rare-earth elements. The build-up of iron is by a factor of 10-17, while the manganese enrichment is even higher. At the same time the phosphorous build-up factor in the nodules is the lowest of all the elements. The reason why this is observed may be found in the growth in the quantity of phosphorous associated with bone apatite, and, alongside the oceanic pelagic sediment, the presence of marine sediment as well. Inasmuch as bone apatite does not occur in the nodules, a reduced value for the phosphorous build-up factor is obtained for the case of pelagic environments when calculating the mobility series of the elements in processes of nodule formation [1].

Because the rate of build-up of the rare-earth elements in the nodules lags behind that of iron, we are led to conclude that the process in which ferrihydroxides precipitate into the nodules from out of the sediment is accompanied not only by a variation in the composition of the lanthanoids, that is, the preferred build-up of cerium and light rare-earth elements, but also by a variation in the magnitude of the Ln/Fe ratio in the nodules relative to that for the sediment (cf. Fig. 4). Though it is entirely possible that the size of the Ln/Fe ratio is overstated in the case of the reactive part of the sediment by at least 10% due to incomplete extraction of the ferrihydroxides, there still remains the problem of accounting for the variation in the build-up of the rare-earth elements relative to that of iron in the sediment and the nodules in view of the obvious relation between the rare-earth elements and iron. Variations in the build-up of the rare-earth elements with respect to that of iron in the nodules becomes possible with the entry of ferrihydroxides, which are absent from the sorbed assemblage of the rare-earth elements. The hypothesis that there occurs an analogous entry of ferrihydroxides from seawater is rather difficult to maintain, since, despite these circumstances, the conditions of sedimentation are, on the whole, reflected in the composition of the sediments, in particular by their reactive part. Consequently, the variation in the Ln build-up with respect to that of the iron occurs following the sedimentation process, but prior to entry of the oxyhydroxides into the nodules.

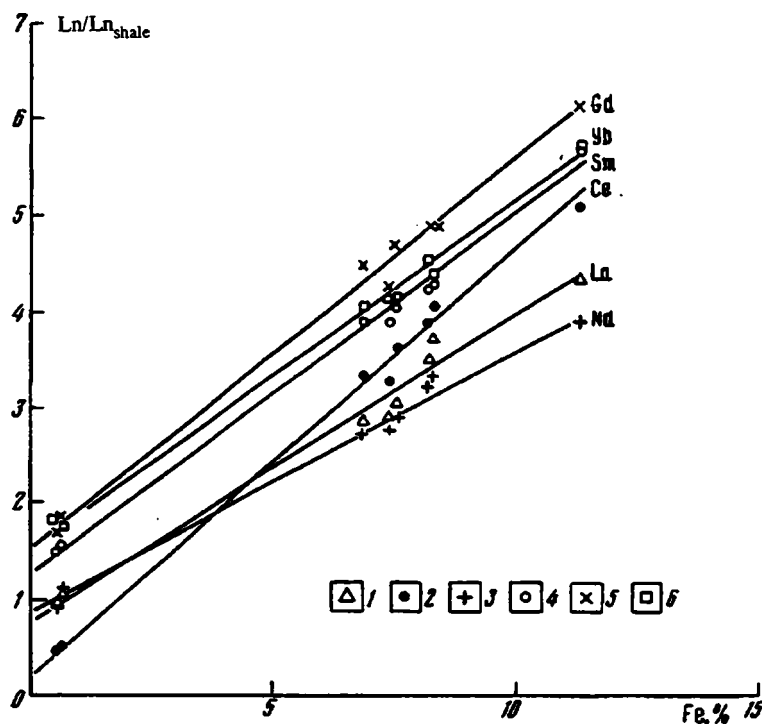


Fig. 4. Dependence of content of rare-earth elements normed by shale (NASC) on Fe in extracts from the sediment and the nodules in column 56. (1) La; (2) Ce; (3) Nd; (4) Sm; (5) Gd; (6) Yb.

The apparent contradiction between the difference in the value of the Ln/Fe ratio in the sediment and in the nodules may be resolved by making use of the data presented in Fig. 4 and in Table 6. Figure 4 illustrates the dependence of the contents of individual rare-earth elements on Fe in Chester extracts from the sediment and nodules in column 56. A practically functional dependence between the contents of the lanthanoids on the iron content is clearly apparent. The regression and correlation coefficients are presented in Table 6. Despite the near functional dependence of the contents of the individual rare-earth elements on iron content (r in the range 0.980-0.999), nevertheless even where the iron content is equal to zero, the content of the rare-earth elements is in no case equal to zero (cf. Fig. 4). Consequently, the reactive forms of the rare-earth elements are not only associated with ferrihydroxides. The content of rare-earth elements that are not associated with ferrihydroxides may be estimated from the size of the free term b in the regression equation for the individual lanthanoids (cf. Table 6), which is expressed by the ratio $\text{Ln}/\text{Ln}_{\text{NASC}}$ (values of Ln_{NASC} are presented in Table 2). Figure 5 presents the composition of rare-earth elements not associated with ferric oxyhydroxides; note that its principal features (negative cerium anomaly and build-up of heavy rare-earth elements) recalls the composition of rare-earth elements that are dissolved in sea water (cf. Fig. 1). Such a composition of rare-earth elements could, potentially speaking, be sorbed by apatite [19]. A second possible source for the rare-earth elements that are not associated with ferric oxyhydroxides could be the sorbed assemblage of rare-earth elements in clay minerals. Data on the rare-earth elements in the clay constituent of sediment were presented in a study by Piper [28] for montmorillonite from the Southern and Northwestern Trough of the Pacific Ocean. The authigenic montmorillonite of the Southern Trough was the only form of montmorillonite containing a weak negative cerium anomaly. Data on the granulometric fractions of the sediment of the pelagic zone of the Indian Ocean, which are entirely represented by clay minerals, attest to the absence of any negative cerium anomaly or build-up of heavy rare-earth elements [29]. Therefore, it is entirely likely that such a composition (cf. Fig. 5) of rare-earth elements is associated with the reactive phase of phosphates (P phase).

The composition of rare-earth elements associated with ferrihydroxides (cf. Fig. 5) is characteristic of the composition of rare-earth elements in hydrogenous ferromanganese deposits of the ocean floor (cf. Figs. 2 and 3). Differences in the composition of the rare-earth elements in the reactive parts of the sediment and nodules from column 56 may, thus,

TABLE 6. Correlation Coefficient (*r*) and Coefficients *a* and *b* in the Equation Expressing the Dependence of the Normalized Content of Rare-Earth Elements in Chester Extracts from Sediment and Nodules of Column 56

Element	<i>r</i>	<i>a</i>	<i>b</i>	Content of rare-earth elements, g/t*		Build-up rare-earth elements on Fe in the oxyhydroxide constituent, mg/t	
				1	2	sediment	nodule
La	0,992	0,321	0,759	10	24	1,1	1,0
Ce	0,997	0,444	0,213	32	16	3,0	3,3
Pr	0,994	0,288	0,815	2,3	6,4	0,24	0,23
Nd	0,994	0,277	0,847	9,1	28	0,83	0,92
Sm	0,997	0,379	1,23	2,2	7,0	0,26	0,21
Eu	0,999	0,394	1,39	0,5	1,7	0,05	0,05
Gd	0,996	0,411	1,51	2,1	7,9	0,21	0,21
Tb	0,993	0,365	1,51	0,3	1,3	0,04	0,03
Dy	0,990	0,371	1,53	1,9	8,0	0,21	0,19
Ho	0,995	0,387	1,66	0,4	1,7	0,05	0,04
Er	0,991	0,318	1,59	1,1	5,4	0,12	0,11
Tm	0,991	0,356	1,51	0,2	0,8	0,02	0,02
Yb	0,998	0,364	1,51	1,1	4,7	0,13	0,11
Lu	0,980	0,342	1,58	0,2	0,8	0,02	0,02

*Calculated contents of rare-earth elements in the Fe phase are scaled on the basis of 1% Fe (1) and in the P phase (2).

be due to the relationship between the contributions of the two constituents, the rare-earth elements associated with the P phase dominating in the sediment, and the rare-earth elements associated with the ferrihydroxides dominating in the nodules. It should be noted here that the content of rare-earth elements associated with the P phase is substantially higher than the content of rare-earth elements associated with the ferrihydroxides, when scaled on the basis of 1% Fe (cf. Table 6). In view of the rare-earth elements found in the sorberd assemblage of sediment, the build-up of lanthanoids on Fe in the oxyhydroxide phase of sediment and nodules as expressed in the Ln/Fe ratio is the same (cf. Table 6). We calculated the rate of build-up using the formula $(Ln - b \times Ln_{NASC})/Fe$, where Ln is the content of lanthanoid in an extract from the sediment, b the free term in the regression equation, and Ln_{NASC} the content of lanthanoid in the shale (cf. Table 2).

The composition of rare-earth elements in the reactive part of the nodules and sediment not associated with ferrihydroxides may reflect the composition of the sorbed assemblage of rare-earth elements in the phosphate. According to the data of Chester and Hughes [13], bony phosphate does not go over into the extract when the sediment is treated with 1 M $NH_2OH \times HCl + 25\% CH_3COOH$. However, in our experiments, which involved leaching (using Chester reagent) samples of shark tooth (growth of K_2m , Crimea; the samples was first pulverized in a mortar) and of apatite with the dimensions of coarse silt (the sample was not pulverized) taken from contemporary oceanic sediment, we were able to show that in the former case 98.5% of the bulk phosphorous ($P_{bulk} = 14.6\%$) went over into the extract, and in the latter case 99.7% ($P_{bulk} = 16.95\%$). In the case of the pulverized samples of sediment both the phosphate ion sorbed on the ferrihydroxides as well as the bony apatite goes over into the Chester extract. Consequently, 0.06 to 0.12% of the phosphorous (according to the difference in the data of Tables 2 and 5) may occur in the composition of fragmentary phosphorous in sediments from the 0-1- and 1-3-cm levels, respectively. Phosphorous that has went into the extract in the sediment is most often a sum of the contents of phosphorous occurring in a composition of ferrihydroxide [8] and bone apatite. Phosphorous from the nodules, by contrast, is sorbed basically on the ferrihydroxides, since it is highly associated with iron (cf. Table 4). Inasmuch as sorption of rare-earth elements on apatite is due to its interaction with phosphate ions [19], the mechanism responsible for the interaction of rare-earth elements with phosphate ions sorbed on the ferrihydroxides may resemble the analogous mechanism for apatite. The formation of the composition of rare-earth elements in the nodules is apparently the result both of the differing mobilities of the ferrihydroxides and iron phosphate as well as the fact that bone apatite cannot be involved in the formation of nodules. The Fe/P ratio in extracts from sediment is in the range 5.1-5.9, growing to 40-50 in the nodules, i.e., it increases by a factor of 8 to 10. If it is supposed that the rare-earth elements

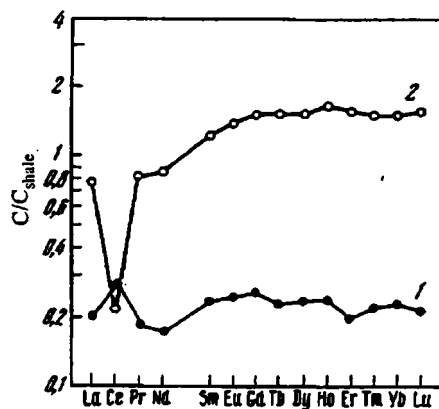


Fig. 5. Compositions of rare-earth elements in extracts from sediments and nodules associated with ferrihydroxides (1) and the P-phase (2).

that are not associated with the ferrihydroxides are instead associated with phosphorous, the growth in the value of the Fe/P ratio for the case of nodules as compared with the value of this ratio for the reactive part of the sediment leads to a build-up in rare-earth elements that are sorbed on the ferrihydroxides by a factor in this range. And this, in turn, changes the composition of rare-earth elements in the nodules, which acquire a positive cerium anomaly while the content of the intermediate rare-earth elements grows (cf. Figs. 2, 3, and 5).

The variations in the manganese content in the sediment core that we referred to earlier indicates that processes of reducing diagenesis must have occurred. Under these conditions manganese could have been reduced to Mn^{2+} and lost its sorbed assemblage of minor elements (Cu and Ni), which could have gone over into ooze. The elevated mobility of manganese, which is due to its reduction, leads to its enriching the upper parts of the nodules. It is possible that the slight enrichment of the upper parts with manganese is a result both of its greater mobility as well as the dominant effect of the ferrihydroxides from the sediment on the lower parts of the nodules.

* * *

1. Oscillations in the macroscopic and microscopic composition of nodules within a single bottom dredge sample were studied for the first time. It was shown that variation in the composition of the nodules is significant both between the upper and lower parts of the each nodule as well as between individual nodules.

2. Ferrihydroxide and manganese oxyhydroxide from the reactive part of the sediment are the source of the ore matter in the nodules.

3. The difference between the upper and lower parts of the nodules reflects differences in the mobility of iron and manganese. The upper parts of the nodules are enriched with manganese as a consequence of the greater mobility of the latter in processes involved in early reducing diagenesis which also affects the sediments. The behavior of copper and nickel is similar to that of manganese. Iron enriches the lower parts of the nodules. Besides iron, the lower parts of the nodules are also enriched with cobalt, rare-earth elements, and phosphorous.

4. The composition of rare-earth elements differs between the nodules and sediment; in the sediment a composition of rare-earth elements is noted that is characteristic of hydrothermal sedimentary deposits in the ocean, whereas in the nodules the composition of rare-earth elements is typical of that observed in hydrogeneous pelagic crust and nodules. Moreover, the mobility of the cerium anomaly in the lower parts of the nodules is greater than in the upper parts.

5. Analysis of the dependence of the rare-earth elements on iron in the reactive portion of the sediment and nodules made it clear that the rare-earth elements in the reactive portion of the sediment are represented in the Fe and P phase. In the Fe phase the composition of rare-earth elements exhibits the features of pelagic crusts and nodules, while in the P phase, it has the composition of rare-earth elements dissolved in pelagic oceanic water. The differing degrees of mobility of these phases in processes involved in the formation of nodules (in the sediments the Fe/P ratio varies in the range 5.1-5.9, while in the nodules, from 40 to 50) is responsible for the differences in the compositions of rare-earth elements of

the reactive parts of the nodules and sediment. In iron-enriched nodules the importance of the Fe phase for the rare-earth elements is amplified (roughly by a factor of 10).

6. Analysis of the build-up in the Ln/Fe form for the Fe phase of nodules and sediment did not demonstrate any differences between the two, showing that sediment was the source of the ferrihydroxides before they entered the nodules.

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GEOLOGICAL STRUCTURE OF THE NORTHEASTERN BALTIC

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UDC 551.35(261.35)

On the basis of seismoacoustic data, echo sounding, and study of cross sections of sediments obtained with the help of coring tubes, the authors consider new information about the composition of sediments and rocks, the structure of the sedimentary layer, bottom relief, and the sub-Quaternary surface in the Northeastern Baltic. The geological map of the region is improved; new faults are revealed, and known ones are confirmed. Several bands of terminal-moraine ridges connected with the known Salpausselkä ridges are outlined. A number of convex sedimentary bodies (such as alluvial fans and channel levees associated with erosion troughs) are revealed, which are a result of the activity of bottom currents.

As a result of geological and geophysical investigations performed in recent decades in the Baltic Sea [2-6, 9, 10, 15, 18, 21], the basic features of the sedimentary mantle's and crystalline basement complex's structure have been revealed; geological, tectonic, structural, and geomorphological maps have been compiled; and the history of development of the Baltic basin has been discussed. However, the greatest part of these investigations is for the Southern and Central Baltic, where prospective oil regions are concentrated [4]. The geological structure of the Northern Baltic, where the pre-Quaternary sedimentary mantle, as the most interesting from the point of view of oil and gas content, is thin or completely absent, has been studied in much less detail. Our knowledge of the geological structure of this region was significantly expanded by geological and geophysical materials obtained in 1988 on voyage 55/11 of the scientific research ship *Shel'f*. Studies were conducted in the northeastern Baltic and in the western part of the Gulf of Finland (Fig. 1) and included taking samples of bottom sediments, continuous seismic profiling (CSP), and echo sounding.

The structure of the sedimentary strata was studied with the help of an electric-spark seismoprofilograph (in the range of recordable frequencies of 60-600 Hz). A two-channel "Omar" echo sounder was used for the same purpose, in which the low-frequency channel (25.5 kHz) gave information about the fine structure of sedimentary bodies in the upper part of the cross section; and the high-frequency channel (145 kHz), about the bottom relief. Columns and samples of bottom sediments were taken with coring tubes (impact and piston-type) and with dredges.

LITHOLOGICAL AND STRATIGRAPHIC COMPLEXES

Seismogeological and Geomorphological Characteristics of the Region. Pre-Quaternary complexes differ in their material composition, physical properties, and internal structure, therefore they show up differently in the acoustic field, in the bottom relief, and in the surface of pre-Quaternary rocks. All of this helps to distinguish (in seismoacoustic sections) crystalline and sedimentary rocks; and in the latter, terrigenous and carbonate components [4].

With respect to the nature of manifestation of the indicated complexes in the bottom relief and the surface of pre-Quaternary rocks in the Northeastern Baltic, we can distinguish two provinces (northern and southern), which also differ sharply in geological structure. A series of benches in Lower-Paleozoic deposits serves as the natural boundary between them (Fig. 2).

Outcrops of many lithological and stratigraphic boundaries to the bottom surface or the pre-Quaternary surface (for example, the boundary between crystalline and sedimentary rocks, and between Cambrian terrigenous and Ordovician carbonate complexes) are frequently accompanied by benches and steep slopes, which makes it possible to positively trace these boundaries between profiles on echograms and CSP sections (see Fig. 3, profiles 8-10).

On the greater part of the echograms, steep slopes and benches, where Cambrian-Ordovician rocks are found, have an almost standard profile (see Fig. 3, profiles 8-10). Its height varies from 50 to 100 m. The steepest and highest bench stretches north of Hijumaa Island and along the coast of Estonia, where it is dissected by canyons and faults.

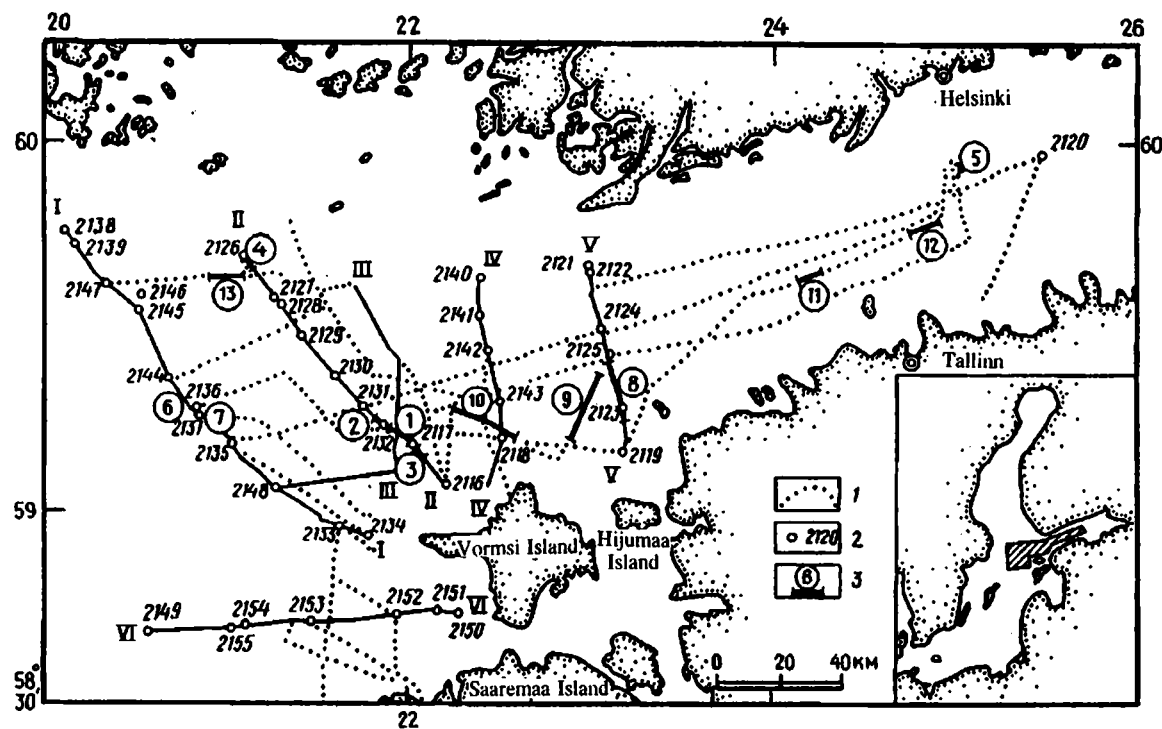


Fig. 1. Diagram of geological and geophysical studies: 1) echo-sounding profiles; 2) geological station and its number; 3) areas of profiles shown in photocopies (see Fig. 3); VI-VI – CSP profiles.

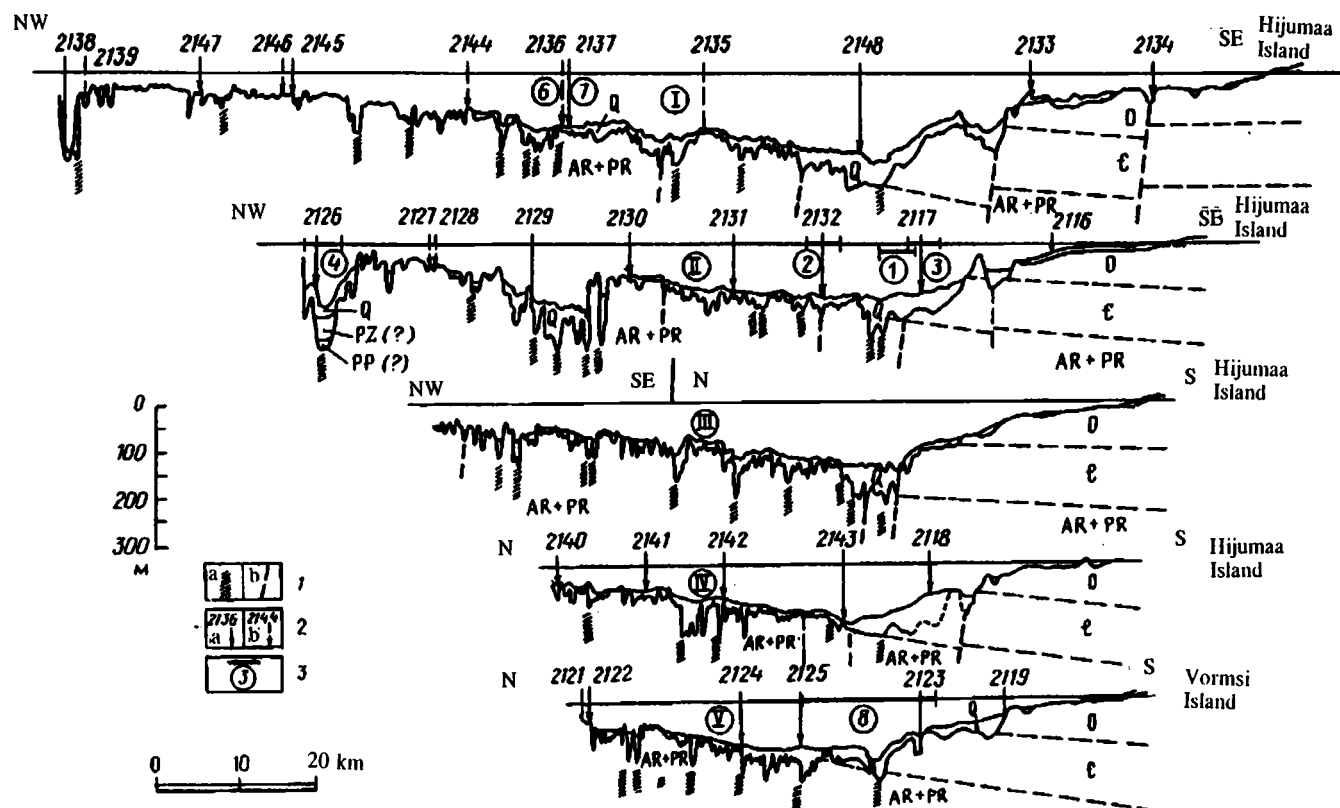
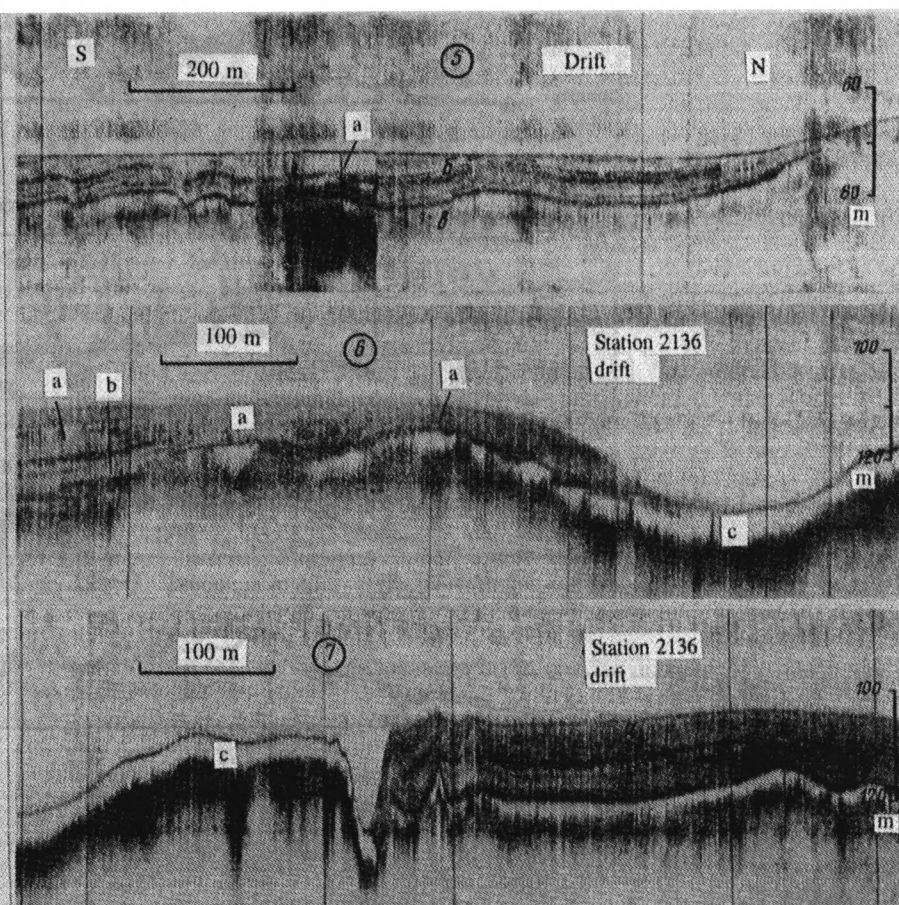
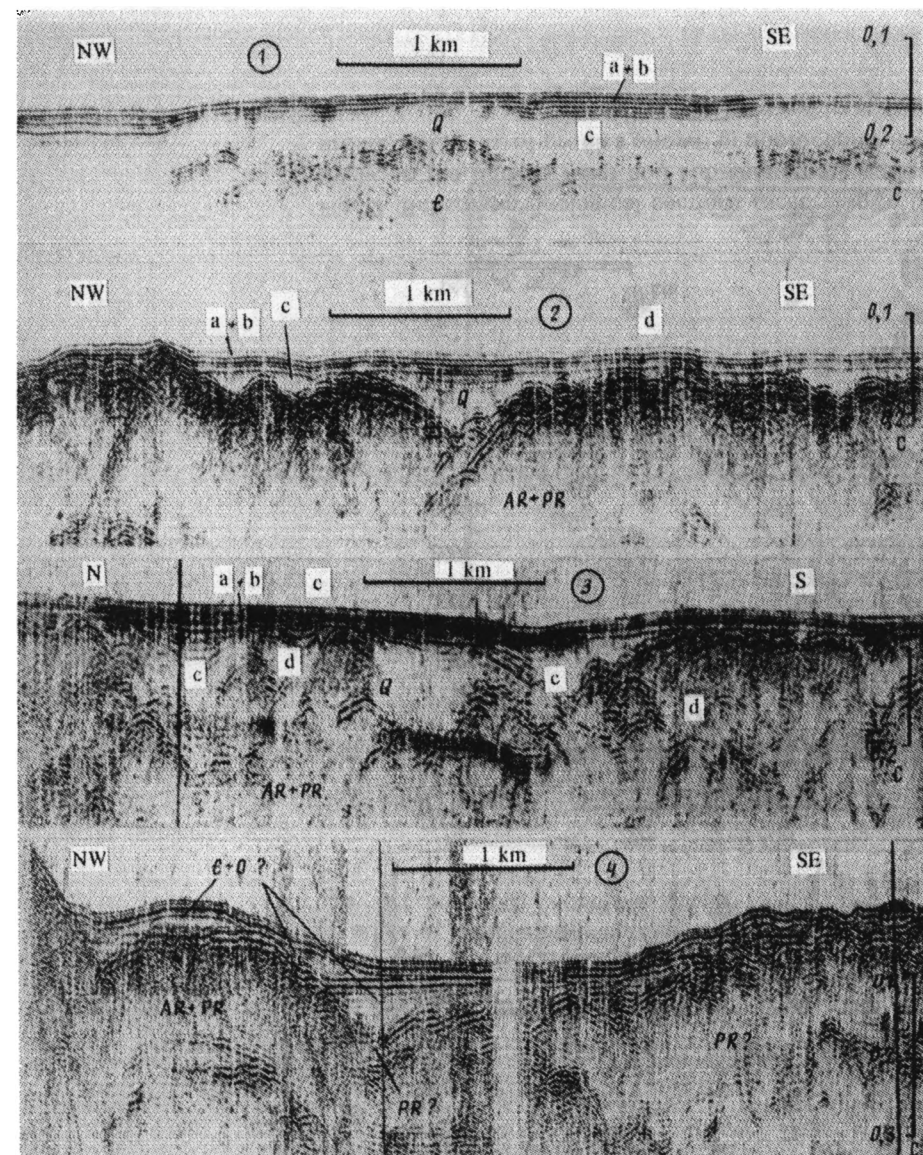


Fig. 2. Schematic geological sections (according to CSP data): 1) faults (a,b – clearly and slightly expressed, respectively, in the bottom relief and sub-Quaternary surface); 2) geological stations (a – on CSP profile, b – alongside of profile); 3) areas of profiles shown in photocopies (Fig. 3).



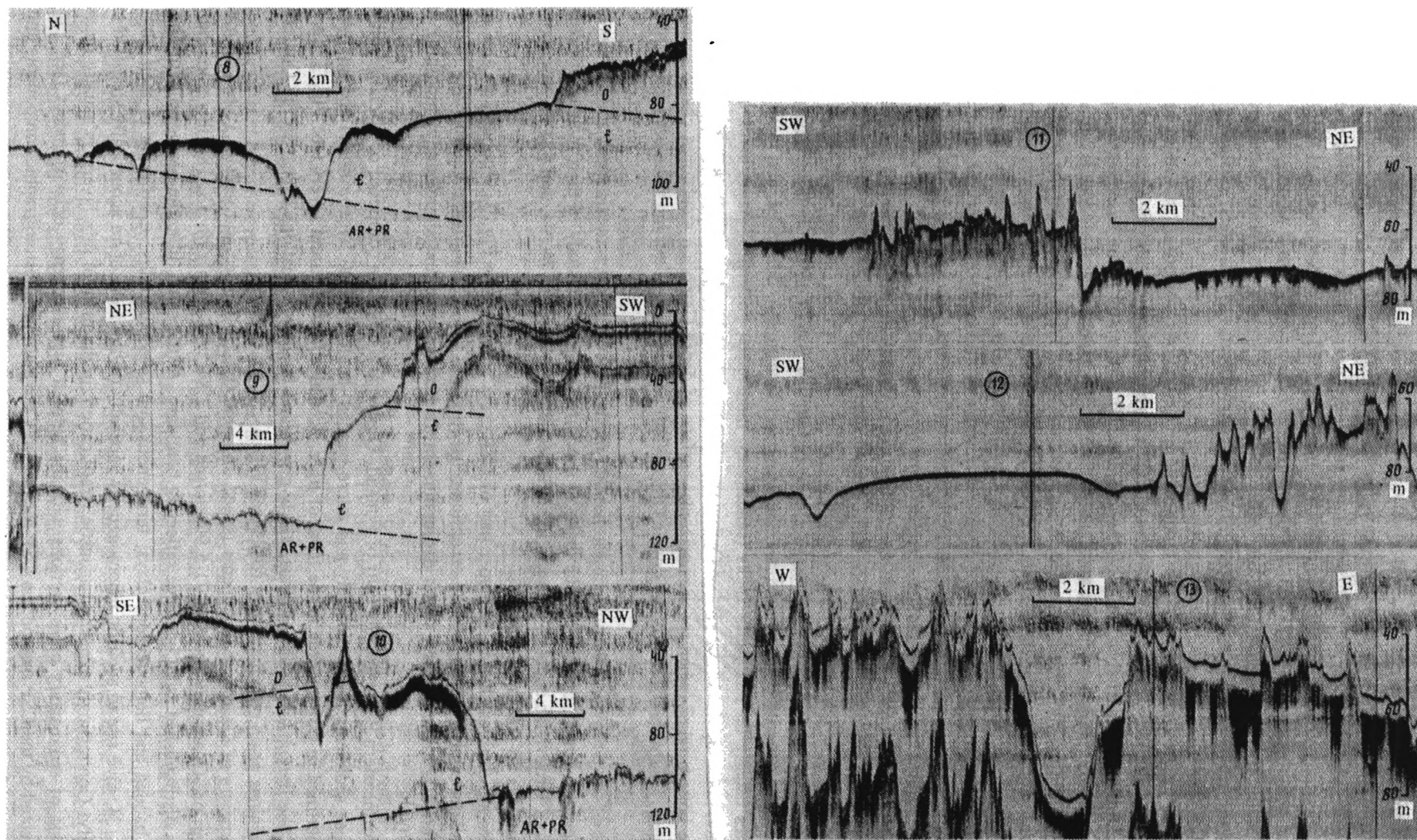


Fig. 3. Examples of seismoacoustic sections and echograms: 1-4) cross sections of Quaternary and pre-Quaternary sedimentary mantle obtained by the CSP method; 5-7) cross sections of loose sediments obtained with an echo sounder; 8-10) bottom profiles in the region of benches; 11-13) examples of faults, canyons, and traces of bottom currents (in the form of sedimentary embankments – channel levees). Age of deposits of rocks and sediments; Q – Quaternary (a – silts of marine genesis, b – hydrotroilitic clays of the transition stage, c – banded and homogeneous clays of lacustrine genesis, d – glacial deposits – moraines); O – Ordovician, € – Cambrian, PZ – Paleozoic, PR – Proterozoic, AR – Archean.

Pre-Quaternary Deposits: In the region under consideration, the pre-Quaternary sedimentary mantle is composed of Upper-Proterozoic (Riphean-Vendian), Cambrian, and Ordovician formations, which can even be found beyond the bounds of the main field in the form of individual spots (in canyons and grabens).

Riphean deposits (sub-Jotian, Jotian) are represented by conglomerates, gritstones, quartzitic sandstones, and siltstones with a total thickness of several hundred meters [4]. They are widespread in the Northwestern Baltic, where they fill grabens of the basement complex [2-4, 18, 21] and, judging from the nature of the wave pattern, may be present in deep canyons (see Fig. 2, profile II; Fig. 3, section 4). *Vendian deposits* (Valdai series) are known in the southern part of the Gulf of Finland, where they include terrigenous strata (gritstones, conglomerates, sandstones, siltstones, clays) with a total thickness of about 200 m [4, 16].

Cambrian deposits are mostly characterized by terrigenous cross sections composed of sandstones, siltstones, mudstones, black shales, and clays [3-5, 16, 18] that possess clearly expressed bedding and high acoustic permeability, which makes it possible to study their internal structure by the CSP method all the way to the basement complex [4].

In seismoacoustic sections, Cambrian deposits are distinguished almost identically: their foot is connected with an uneven reflecting boundary, and their roof is accompanied by an erosion surface lying under a strong reflector connected with the terrigenous-carbonate contact in Ordovician strata composed of quartz sandstones, limestones, and marls [4].

The region of occurrence of these deposits is frequently accompanied by benches or steep slopes (see Fig. 3, profiles 8-10) formed in strongly cemented sandstones [4]. In the absence of such, the boundary of their occurrence is noted according to a change in the wave pattern, bottom relief, and the surface of pre-Quaternary rocks (replacement of an unbedded cross section by a bedded one, and of dissected relief forms by smoothed-out ones).

The thickness of Cambrian deposits in wells on land (File-Haider, Gotska-Sande, Kingisepp) is equal to 80, 157, and 113 m, respectively [4]. In the region of the Northern Baltic under consideration, according to CSP data it is estimated as 100-130 m.

Ordovician deposits form steps, benches, or steep slopes (20-30° or more) in the bottom relief, from which dredging lifted up specimens of carbonate rocks: limestones (including reef limestones), dolomites, and marls [4,5]. At the bases of slopes and benches usually lie sandy-clay rocks (sandstones, mudstones, siltstones, clays, black shales) with a thickness of 20-30 m, which make up the lower part of Ordovician cross sections [4]. In echograms (see Fig. 3, profiles 8-10), the inflection in the bottom relief (when the subhorizontal surface of dense Cambrian sandstones changes into the inclined surface of less dense, sandy-clay rocks of the Lower Ordovician) corresponds to the interface between Cambrian and Ordovician deposits.

Carbonate deposits of the Ordovician (mainly limestones and marls) possess slight acoustic permeability, therefore they often form acoustic screens, which, by reducing the depth of sounding, hamper the study of their internal structure.

The total thickness of Ordovician deposits in the wells indicated above is equal to 74, 94, and 124 m, respectively, while in the Northern Baltic it is 80-100 m [4, 18].

Quaternary deposits are distinguished in the upper part of CSP cross sections (see Fig. 3, sections 1-4) and cover almost the whole surface of underlying rocks, with the exception of steep slopes and individual elevations. They lie on the pre-Quaternary base with angular unconformity, filling depressions in the ancient relief and significantly smoothing them out.

In basins of the Northeastern Baltic and the Gulf of Finland, Quaternary strata are composed of glacial formations (moraines) covered by loose sediments: clays (coarsely and micro-banded, homogeneous, hydrotroilitic) and terrigenous silts (Fig. 4), which are outlined in CSP records in the form of light, acoustically transparent layers (see Fig. 3, sections 1-4). In elevated areas of the bottom and south of clints, sandy-gravel and boulder formations appear in the Quaternary cross section, lying on moraines or on pre-Quaternary rocks (see Fig. 4).

The acoustic parameters of Quaternary sediments (speed of sound 0.3-2.0 km/sec and density 1.06-2.30 g/cm³) differ sharply from those in pre-Quaternary rocks (1.71-5.90 km/sec and 1.84-2.93 g/cm³) [8, 13, 18], therefore the foot of the Quaternary strata is distinguished as an intensive reflecting boundary. At the same time, the components of Quaternary strata — moraines, banded and homogeneous clays, terrigenous and sapropelic silts — differing in their physical properties themselves [8, 13], give rise to acoustic inhomogeneity vertically (in the form of an acoustically stratified cross section), as well as laterally. Contrastingly expressed acoustic stratification (in the form of thin layers) is usually recorded in the upper (0-30 m) part of sedimentary cross sections with the help of high-frequency echo sounders (see Fig. 3, sections 5-7). It is not detected by the CSP method; on CSP records only the main seismostratigraphic components and the boundaries or unconformity surfaces separating them are seen.

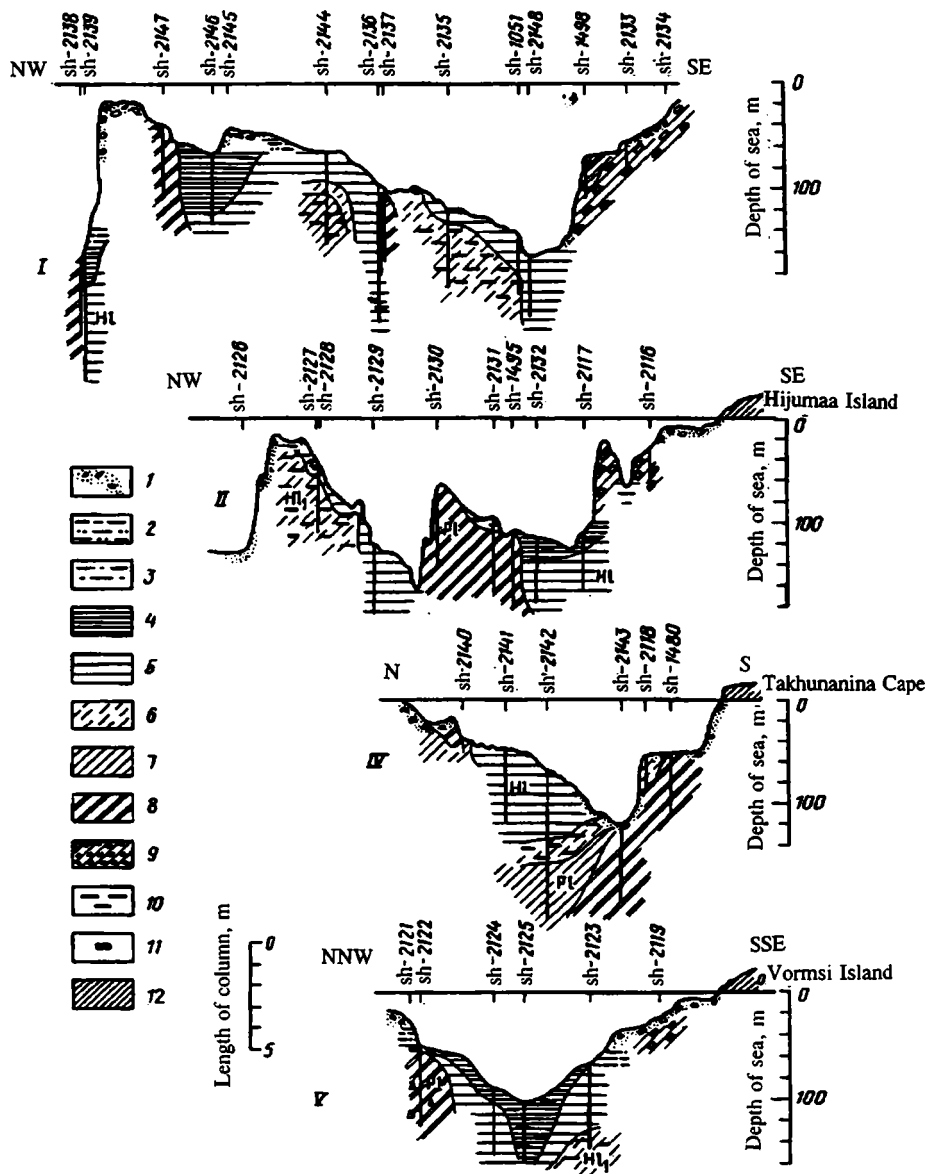


Fig. 4. Schematic lithological-stratigraphic sections compiled according to data from taking samples (stations of other expeditions were also used): 1) sand, gravel, pebbles; 2) coarse siltstone; 3-5) silt (3 – fine-silty, 4 – pelitic, 5 – pelitic microlayered); 6-8) clay (6 – gray, 7 – brown, 8 – banded); 9) moraine loam; 10) hydrotroilite; 11) ferruginous crusts; 12) dry land. See Fig. 1 for the cross sections' location.

The thickness of Quaternary deposits varies in a very wide range (0-90 m), reaching maximum (30-90 m) values in deep notches. Over the greater part of the area it is 0-20 m (with a predominance of 5-10 m).

Pleistocene glacial deposits are represented by moraines lying at the base of the Quaternary strata. There are most often brownish-gray loams with pockets of fine-grained sand, and fragments of limestones and granitoid rocks. In their physical properties and internal structure (chaotic reflections, lenticular-imbricate form of the bodies), they differ significantly from the covering clays and underlying rocks.

The roof and foot of the moraines form strong and uneven reflecting boundaries, which makes it possible to almost unequivocally distinguish them in the Quaternary sedimentary section. Only in areas where the underlying surface is heavily dissected, and the thickness of the moraines is small (at the limit of the CSP method's resolution), are they

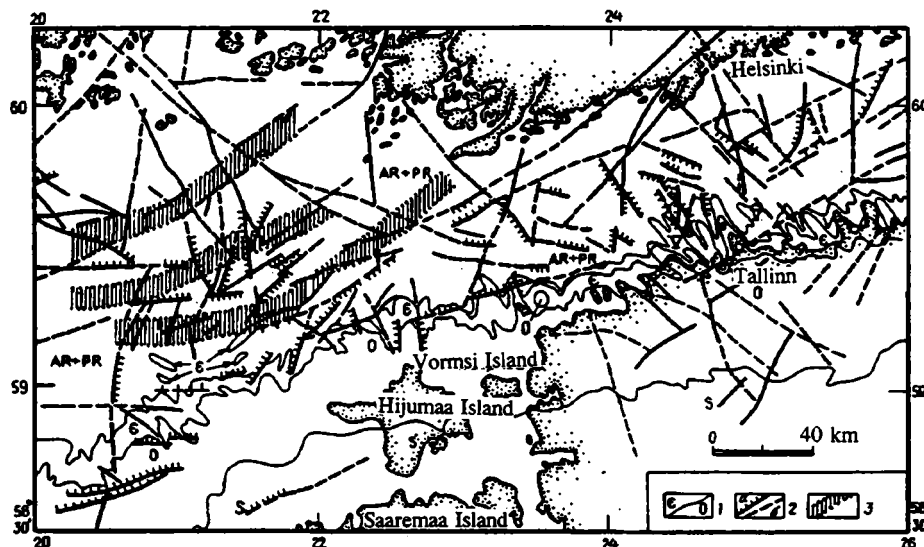


Fig. 5. Schematic geological map: 1) stratigraphic boundaries; 2) faults (a,b – with established and unestablished displacement elements, respectively); 3) zones of increased thickness of moraines.

ambiguously distinguished, since reflections from the roof and foot run together. In places where moraines are eroded, the bottom surface is uneven, and reflections from the bottom are strong. For a high-frequency echo signal, the surface of moraines is an acoustic screen.

Judging from CSP data, moraines are not found everywhere. Lenses of moraines 20–40 m thick are detected in the band in front of clints (west of station 2133, near station 2117, north of station 2143, south of station 2125) in deep notches and on their slopes. Increased thicknesses of moraines (see Fig. 3), which correlate between profiles, are most likely connected with terminal-moraine ridges. Three such ridges, gravitating toward faults and nodes of their intersection, are traced in the northwestern part of the region under investigation (Fig. 5), where they coincide with the Salpausselkä terminal moraines revealed there previously [17, 20].

Signs of moraines (in the form of local elevations) are also noted west of Hiiumaa Island, where they are eroded and covered with sand, pebbles, and boulders. Judging from data on the lithological sections (see Fig. 4), moraines in the form of a thin layer (several meters thick) blanketing the preglacial relief may be much more widespread; however, on the strength of the limited resolution of the CSP method, we are unable to establish this.

Pleistocene clays and Holocene clays and silts represent loose sediments that, in comparison with moraines, are found over almost the whole area. In basins of the sea, they account for the predominant part of the Quaternary cross section or the whole cross section (see Fig. 3, section 1).

Banded and homogeneous clays (Upper Pleistocene–Lower Holocene) lying at the base of loose sediments are frequently found on the bottom surface, due to erosion (see 2130, 2131, 2143, 2147). They are usually light-brownish-gray, plastic, and dense. At low and high frequencies, they are recorded in the form of an acoustically transparent layer – a brightened band (see Fig. 3, layer c) blanketing the relief of the underlying surface. The roof of the clays (mostly banded ones) is usually distinguished as a strong reflecting boundary, which is frequently the surface of angular unconformity or erosion. Therefore, in regions where clays are exposed, reflections from the bottom become more contrasting in comparison with adjacent areas covered with terrigenous silts.

Significant differences in the physical properties of silts and clays [8, 13] lead to a situation in which the surface of banded clays (especially coarsely banded ones) becomes an acoustic screen for high-frequency echo signals. This screen, separating the upper, acoustically strongly stratified layer (see Fig. 3, layer a + b) and the lower, unstratified one (layer c), is recorded by the echosounder in almost all basins of the Baltic Sea [10] and may be connected with the surface of carbonate banded clays.

The clays' total thickness is 0–10 m, although in notches and basins it can reach 60 m. On elevations and in notches, where loose sediments are subjected to erosion, banded clays are frequently covered with a thin (0–10 cm) layer

of quartz-feldspar sand (see Fig. 4, stations 1480, 2147, etc.). Traces of erosion of sediments and outcrops of banded clays are noted in canyons of the Northwestern Baltic (see 2138 and 2143).

In basins of the sea (at a depth of 80-160 m), banded and homogeneous clays are covered by Holocene, hydro-troilitic clays and terrigenous silts filling depressions in the underlying surface. In the region of occurrence of silts, a leveled bottom is noted, and reflections from the bottom are weak (without repeated waves). The most extensive field of silts gravitates toward the basin near a clint (see Fig. 4), which serves as one of the zones of accumulation of sedimentary material.

In many places, terrigenous dark-gray (on black) silts are gas-saturated (stations 2125, 2129, 2132, 2146, etc.), contain hydrotroilite (in the form of clumps, lenses, and interlayers), and strongly absorb and dissipate acoustic energy. Areas of absorption and dissipation are recorded on echograms in the form of dark or light spots and indicate sharp attenuation of the signal's amplitude and a reduction in the depth of sounding. Dissipation of acoustic energy on local inhomogeneities (for example, on gas bubbles or concretions of hydrotroilite) leads to darkening of the seismoacoustic section under the dissipating object, and to formation of a vertical tail ("beard"), therefore a dark record with signs of dissipation of waves is usually characteristic of gas-saturated silts, and also of clays with inclusions of hydrotroilite.

Hydrotroilitic clays are separated from the covering terrigenous silts by a weak and intermittent boundary (see Fig. 3, sections 5-7); in many cases, clays and silts merge into a unified layer, the thickness of which is estimated as 0-20 m (more often 3-4 m), reaching maximum values in basins.

Gassiness of the bottom layer of sediments intensifies reflection from the bottom and (in the case of gas flows) leads to formation of funnels and little craters on the bottom [11, 19]. Since gas can have near-surface (diagenetic) or deep origin, dark and light spots on seismoacoustic sections can serve as an indirect indicator of faults or accumulations of organic matter in buried paleonotches.

In shallow-water areas of the bottom (depths less than 30 m), the upper part of the Quaternary cross section is represented by Holocene and contemporary quartz-feldspar sands or coarse siltstones (from several centimeters to several meters thick), which are products of erosion of moraines, the pre-Quaternary bed, or brought in by currents from other regions. Strong, repeated reflections are recorded from the surface of coarse-grained deposits.

North of clints, on elevations and in depressions of the bottom, quartz-feldspar sands of medium and varying grain size sometimes lie in a thin layer (from 1 cm to tens of centimeters) directly on silts (see Fig. 4, station 2128) or banded clays (stations 2143, 2130, 2147). South of the clints, sandy deposits cover almost the whole carbonate plateau, lying on pre-Quaternary rocks, moraine loams (see 2116, 2133), and banded clays (see 1480, 1498). The stiff bottom, repeated reflections from the bottom, and samples of sand taken with a dredge (for example, at station 2143) in canyons indicate that sands may line the bottom of deep canyons in the Northeastern Baltic, and these canyons themselves serve as channels for bottom currents.

The existence of bottom currents in the Northern Baltic is indicated not only by deep erosion channels (canyons) with a sandy bottom, but also by the convex shape of sedimentary bodies (reminiscent of alluvial fans and channel levees) associated with adjacent erosion troughs (see Fig. 3, profiles 6, 11, and 12). CSP data show that the heavily dissected relief of the underlying surface is buried under these bodies. A convex shape of sedimentary bodies is also found on the bottom and sides of notches, and on basin slopes, where the bottom is composed of loose sediments that do not give repeated reflections. This may indicate finer-grained (silty) material deposited there as a result of the low velocity of bottom flow.

These sedimentary bodies with a convex shape are noted in a band in front of clints (at depths of 120-160 m), in the axial part of the Gulf of Finland (60-80 m), and in canyons of the Northeastern Baltic (100-150 m). The presence of such bodies may indicate contour currents [12] in the Northern Baltic and Gulf of Finland, oriented along the coasts and axial zone of this gulf.

THE ROLE OF TECTONIC MOVEMENTS IN FORMATION OF THE SEDIMENTARY MANTLE

The region of the Northern Baltic under investigation is in the junction zone of the Baltic shield and the Russian platform [2, 4, 9, 16], where the basement complex is broken up by numerous dislocations (see Fig. 5), and its surface, bending, begins to plunge steeply to the south (see Figs. 2 and 5). This inflection coincides with the axial zone of the Gulf

of Finland and its western continuation. At the boundaries of the Paleozoic sedimentary mantle, the surface of the basement complex reaches absolute elevations of -120 to -250 m.

Over the greater part of the area under consideration, the basement complex is covered by a thin (average 5-10 m) layer of Quaternary deposits, therefore all of its tectonic elements are reflected in the bottom relief and the sub-Quaternary surface. Fractures in the basement complex worked by erosion and exaration processes show up here in the form of faults, benches (50-80 m high), and canyons (see Figs. 2 and 3, profiles 11 and 13). The deepest canyons in the Northeastern Baltic (60-140 m deep) were cut along tectonic zones known there (see Fig. 4, region of stations 2126 and 2138).

Among the complex mosaic of dislocations, two systems of faults with different orientation are distinguished: diagonal (northeast-southwest and northwest-southeast) and latitudinal-meridional. Faults of the diagonal system are expressed most contrastingly, occur everywhere, and are traced over many tens of kilometers (including in the territory of Finland and Estonia).

Faults with a northeast-southwest orientation were established in Precambrian time, together with the origin of the Gulf of Finland's basin [2, 4, 6, 9], and over the course of the Phanerozoic they experienced more than one activation. They made the main contribution to development of this basin and the southeastern margin of the Baltic shield, determining the trend of Paleozoic sedimentary complexes. Neotectonic and glacioisostatic activation of them was expressed in the analogous trend of the whole coast of the Gulf of Finland, bottom benches, and also the isobaths of contemporary uplifts of the Earth's crust [3].

Faults with a northwest-southeast orientation also have a Precambrian origin and, together with dislocations with a different trend, experienced neotectonic activation [6, 9]. In many places, they were manifested in the form of zones of tectonic jointing (widespread in the sedimentary mantle of Northern Estonia [14]), along which deep canyons were incised as a result of intensive exaration and erosion. Faults with this trend were manifested mainly in local relief forms of the bottom and the sub-Quaternary surface, sections of the coastline of Estonia, and adjacent islands.

Faults of the latitudinal-meridional system are concentrated primarily in the western part of the region, where they are contrastingly expressed and fairly extended; in other areas, these dislocations are traced locally. They conform to the trend of mostly local forms of the coastline, and the boundaries of occurrence and isopachs of Paleozoic sedimentary complexes, which is an indication of these faults' activity during Caledonian, as well as neotectonic and contemporary movements.

Neotectonic movements and subsequent glacioisostatic uplift of the Baltic shield activated all of the tectonic zones (especially faults with northeast-southwest and sublatitudinal orientations, which possess the greatest spread of amplitudes) and provoked local earthquakes [1, 7]. The lowered northern limbs of sublatitudinal faults only reflect the mechanism of tension of the Earth's crust on the slope of the rising Baltic shield. Movements of blocks of the basement complex along faults in the shield's marginal zone determined the regional trend of the coastline and terminal moraine ridges in this region. The coincidence of some faults with benches indicates a significant contribution of the tectonic factor (along with erosion and exaration) to their formation.

Neotectonic and contemporary movements of the Earth's crust, by causing uplift or lowering of blocks of the basement complex, created the prerequisites for formation of straits and obstacles for the flow of Baltic waters. Thanks to straits (which promoted penetration of saline North Sea waters into the Baltic body of water), the Baltic basin became a slightly salty sea; the emergence of obstacles in the way of water flow transformed it into a closed, freshwater lake.

In the history of development of the Baltic Sea, several such transformations (stages) are known [3]. The transition from one stage to another was accompanied by particular geological events (fluctuations in sea level, changes in the body of water's hydrochemical regime and sedimentation conditions, and the material composition and physical properties of sediments), which left traces in the sedimentary mantle in the form of separate structural and lithological complexes, and strong reflecting boundaries or surfaces of angular unconformity and erosion. According to CSP data, three structural complexes are outlined in the cross section of loose sediments, separated by unconformities. They differ in their internal structure and correspond to three basic stages of the Baltic body of water's development.

The lower (acoustically homogeneous laterally) structural complex, which is mainly represented by banded clays blanketing irregularities of the bed, was formed in a lacustrine stage with a weak hydrodynamic regime, while the upper, strongly stratified complex (terrigenous hydrotroilitic and sapropelic silts), which fills depressions in the underlying surface, reflects a marine stage of sedimentation with well developed bottom currents. In the intermediate complex separating them (hydrotroilitic clays), a gradual transition from blanketing structures to filling ones is noted, i.e., from the lacustrine stage to the marine one.

In conclusion, we should note that the geological structure of the Northeastern Baltic differs significantly from more southern regions. The crystalline basement complex in northern regions emerges to the pre-Quaternary surface, therefore its faults are directly reflected in the bottom relief and in the configuration of the coastline, and can be studied by geomorphological, as well as geophysical methods, while in southern regions the basement complex is lowered many kilometers. The greater part of its faults fades out there in the sedimentary mantle, showing up in the upper part of the cross section only indirectly, in the form of flexures, zones of jointing, and inherited notches remote from the main faults [9].

In the Northeastern Baltic, movement of blocks of the basement complex along faults was directly reflected in the structure of Quaternary deposits (in the form of structural complexes, displacement of layers, zones of jointing, and inherited notches). Above faults, numerous gas-flow channels formed there, which are recorded in the form of acoustic anomalies [19]. In more southern regions, where the energy of mechanical movements of the basement complex is absorbed and dissipated by multikilometer sedimentary strata, we only have slight, mediated reflection of faults of the basement complex in Quaternary deposits, in the form of indirect traces: the indistinct outlines of regional relief forms of the bottom and coastline.

The pre-Quaternary sedimentary mantle here forms zones of wedging-out a few hundred meters thick, while in southern regions its thickness increases by almost an order, and carbonate and sandy components in Lower-Paleozoic cross sections are replaced by more clayey ones to the south [3, 4]. There is also a significant difference in the structure of Quaternary deposits. Thus, the thickness of Quaternary deposits in the Northern Baltic is almost an order higher (mostly on account of loose sediments) than in the Middle or Southern Baltic. This is explained by the higher rate of sedimentation in northern regions, where filling of small, but deep basins took place as a result of intensive erosion of moraines and the subglacial bed on the slope of the rising Baltic shield. Thanks to the direct action of movements of blocks of the basement complex on the sedimentation process, the internal structure of Quaternary strata in the north is more contrastingly expressed than in the south, and the increased number of layers in the cross section of loose sediments in northern regions (in comparison with southern ones) indicates more frequent changes in sedimentation conditions.

The investigations that were performed provide a basis for considering that, in its general features, the late- and postglacial evolution of the Northeastern Baltic remained the same as in other regions. This is directly indicated by the identity of the material composition and internal structure of Quaternary cross sections. However, in the Northern Baltic lithological and structural analogs were formed much later than in southern regions. The thick moraine layers revealed here, lying on the continuation of the Salpausselkä terminal-moraine ridges on dry land, are later formations (they arose in the stage of the glacier's recession and degradation) than in southern regions, where the analogous marginal forms are most often connected with the oncoming glacier in early stages of glaciation [3].

Data from the investigations confirmed the repeated tectonic activation of ancient faults, which was intensified in the contemporary period in connection with isostatic uplift of the Baltic shield. In early stages, this activation was reflected in the structure of the Lower-Paleozoic sedimentary mantle and in the trend of its lithological complexes; and in the stage of the latest movements, in the structure of Quaternary deposits and in the orientation of linear elements of the bottom relief and coastline. The tectonic factor played a leading role in establishing the main forms of bottom relief, while erosion and exaration processes accompanying it (manifested with the greatest strength along tectonically weakened zones) only complicated these forms, giving them their contemporary appearance.

Late- and postglacial movements of the Earth's crust found reflection in the structure of Quaternary deposits in the form of individual structural complexes and the surfaces of angular unconformity and erosion separating them, which are frequently connected with strong reflecting boundaries. Individual stages (lacustrine, marine) of the Baltic body of water's development are imprinted, as it were, in the Quaternary sedimentary mantle. Thanks to intensive hydrodynamic processes, the contemporary marine stage of the Baltic basin, which is recorded in the upper structural complex (in the layer of silts), is leaving its traces in the form of erosion and accumulative forms that are the main signs of bottom currents circulating along benches of the northern coast and the axial zone of the Gulf of Finland.

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ISOTOPIC AND GEOCHEMICAL PECULIARITIES AND AGE OF UPPER-PRECAMBRIAN DEPOSITS IN THE WESTERN PART OF THE SIBERIAN CRATON

V. I. Vinogradov, B. G. Pokrovskii, A. M. Pustyl'nikov, V. I. Murav'ev,
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The authors conducted isotopic investigations of Upper-Precambrian deposits in the Katanga saddle. It was shown that the rocks were subjected to strong secondary (epigenetic) transformations. Two stages of secondary transformations were dated: according to glauconites and sltstones. A serious discrepancy was discovered between isotopic and stratigraphic ages.

Study of the isotopic composition of elements in rocks of carbonate cross sections opens fundamental possibilities for judging the conditions of carbonate accumulation. Carbonates are deposited in equilibrium with seawater, and the isotopic composition of elements in them either directly corresponds to the isotopic composition in seawater, or is displaced in relation to it by an amount conforming to the coefficient of isotopic fractionation. This is also true of another class of chemogenic sediments: evaporites, anhydrites in particular. In turn, the isotopic composition of elements in seawater is functionally related to geochemical peculiarities of the global cycle of matter in the "continent-ocean" system. Therefore, isotopic data are an important indication of geochemical situations in the geological past. They are especially significant for Precambrian deposits, where sometimes they are the only objective indication of global conditions of the atmosphere and hydrosphere, and of changes in them in time.

Interpretation of isotopic data, however, is complicated by several circumstances. First, all rocks, and especially readily soluble ones such as carbonates and sulfates, are subject to secondary epigenetic changes, which can distort their original isotopic composition. Consideration of these distortions is extremely complex, perhaps not even always possible, and, in any case, it requires very detailed investigations.

Another hindering factor is the complexity of time correlations of cross sections being studied. In the Phanerozoic, the biostratigraphic method is used. In the Precambrian, it works, if at all, with much less resolution, and correlation of the subdivision of Precambrian sediments is based on methods of isotopic dating, which, in turn, are poorly applicable to sedimentary rocks. Nonetheless, isotopic and geochemical study of the rocks of Precambrian cross sections in various regions of the world attracts the attention of many researchers. The Siberian craton is a unique region for investigations. Thick strata of Precambrian carbonate deposits are developed there, encompassing three erathems of the Riphean [2, 30, 38].

Previously conducted study of Upper-Precambrian carbonates of the Western Anabar region [22] revealed hard-to-explain peculiarities in the distribution of oxygen, carbon, and strontium isotopes in the cross section of Riphean carbonates on the western plunge of the Anabar shield. The present investigation was a continuation of these works being carried on in the laboratory of isotopic geochemistry and geochronology within the framework of the problem "Most important biotic and abiotic events in geological history." We mainly studied cross sections of Riphean deposits from several exploratory (for oil and gas) wells drilled in the Katanga saddle. The choice of this region specifically was determined by the circumstance that one of the wells there disclosed strata of anhydrite rocks in deposits of the Middle Riphean. A find of sedimentary anhydrites at that age level is presently a great rarity.

GEOLOGICAL AND LITHOLOGICAL CHARACTERISTICS OF THE CROSS SECTIONS

Overall Structure of the Cross Section. Structurally and tectonically, the Katanga saddle is located between the Baikit and Nepa-Botuoba anteklises in the southwestern part of the Siberian craton (Fig. 1). The sedimentary mantle

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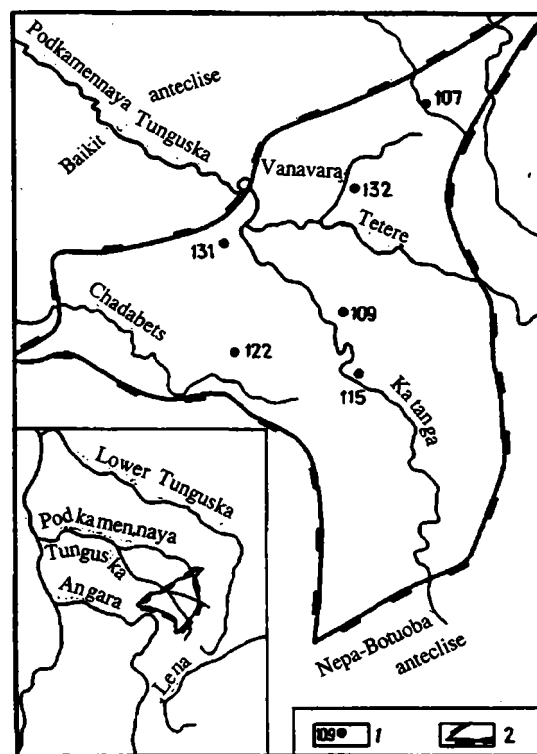


Fig. 1. Diagram of location of studied wells in the area of the Katanga saddle in the territory of the Siberian craton: 1) location of the well and its number; 2) contour of the saddle.

within the bounds of the saddle consists of deposits of the Riphean, Vendian, and Lower Paleozoic. In the last decade, the Soba oil and gas field has been opened there, which is localized in terrigenous deposits of the Vendian. There are also signs of oil and gas content in Riphean, Vendian, and Lower-Cambrian deposits.

The craton's basement complex is composed of highly metamorphized deposits of the Upper Proterozoic-Archean. Rocks of the basement complex crop out within the bounds of the Aldan and Anabar shields. The age of the last magmatic and metamorphic events recorded in them is about 2 billion years [9, 12, 13, 21, 40].

The total thickness of Riphean deposits in the saddle reaches 1700 m (Fig. 2). Two large sedimentary series are distinguished in the Riphean cross section [17]: a lower (Ognev), carbonate-terrigenous one, and an upper, dolomite and clay-dolomite one comparable with the Kamov series of the Baikit antecline. Deposits of the lower complex are developed in the eastern part of the Katanga saddle. They are dated by the potassium-argon method, according to globular glauconite isolated from glauconite-quartz sandstones of the upper, terrigenous strata of the Ognev series in wells 107, 132, and 109 (see Fig. 2), as Middle Riphean – 1230-1265 million years old [18]. According to peculiarities of the rocks' composition, the Ognev series is subdivided into three parts. The lower one of them is represented by green siltstones with occasional interlayers of dolomites and dolomitic breccias and has a thickness of ~175 m. The middle part is dolomite-clay; at its base there is a thick (50 m) horizon of sedimentation dolomitic breccias; the overlying part of the cross section is composed of alternating layers of dolomites and mudstones. The thickness of the strata is 250 m. The upper (terrigenous) strata are alternating dark-green mudstones, quartzitic siltstones, and green glauconite-quartz sandstones with lenses and interlayers of siderite. Their incomplete thickness to the eroded upper boundary is 100-200 m.

Deposits of the Kamov series belong to the Upper Riphean, which is indicated by numerous identifications of microfossils [25, 26]. Potassium-argon datings according to glauconite performed for the Kamov series in the territory of the Baikit antecline, in the Upper Riphean included in a unified structural and formational zone with the Katanga saddle, lie in the range of 1060-1080 million years [17]. The Kamov series is subdivided into four lithofacial complexes (from the bottom up): a sulfate-containing dolomite one with thickness of more than 100 m, with numerous strata, lenses, and

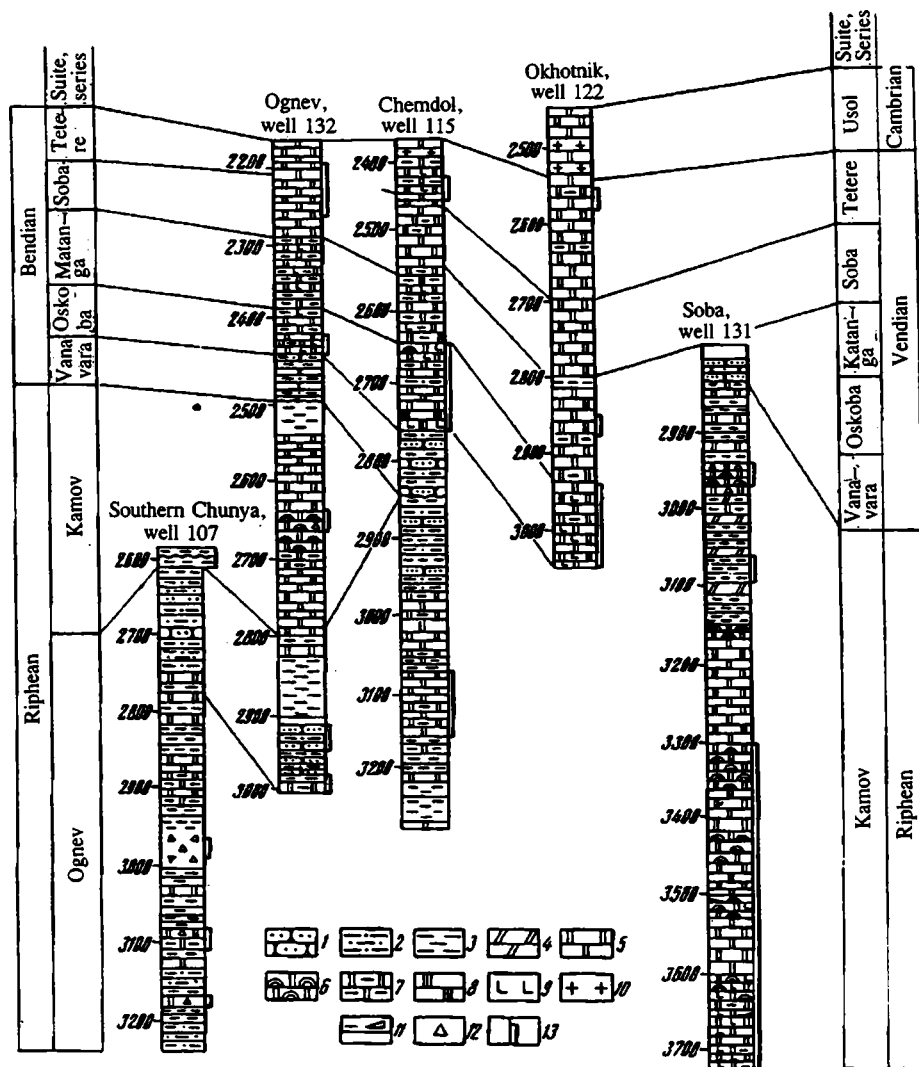


Fig. 2. Composition and structure of Riphean and Vendian deposits of the Katanga saddle: 1) sandstones; 2) siltstones; 3) mudstones; 4) dolomitic marls; 5) silty, clastic, and recrystallized dolomites; 6-7) dolomites (6 - phytogenic, 7 - clay); 8) magnesites; 9) anhydrites; 10) rock salts; 11) siliceous rocks; 12) breccias of various compositions; 13) sampling intervals; the numbers to the left indicate depth from the surface, m.

pockets of anhydrite; a siliceous-dolomite complex with abundant layers and lenses of siliciliths and siliceous stromatoliths, ~450 m thick; a clay one, composed of black clay shales to a significant degree, with interlayers of dolomitic marls, thickness 130 m; and a clay-dolomite one 150 m thick, at the base of which a member of dolomitic breccias is located. The weighted average concentration of organic carbon in Riphean dolomitic rocks is ~0.15% on the whole. In the upper part of the Kamov series' cross section, brownish, recrystallized, slightly bituminous dolomites are fairly widespread. Increased (up to 1.3%) contents of organic carbon are confined to the clay lithofacial complex and interlayers of dark clay shales and dolomitic marls in the clay-dolomite complex. If one takes into account that black clay shales are enriched with diagenetic pyrite up to 5-6%, then the primary (original) concentrations of organic matter in the clays may have reached 10%. On various horizons of Riphean deposits, the Vendian complex lies with erosion; in material composition it is divided into three parts: a lower, terrigenous one; a middle, transitional, sulfate-terrigenous-carbonate one; and an upper, primarily carbonate part. In the studied territory, Vendian deposits are subdivided into five suites, each of which has a thickness in the range of 6-150 m [19, 27]. Terrigenous deposits are isolated in the Vanavara suite, which is composed of interbanded quartz and feldspar-quartz sandstones, quartz siltstones, and mudstones. The clastic rocks' cements are

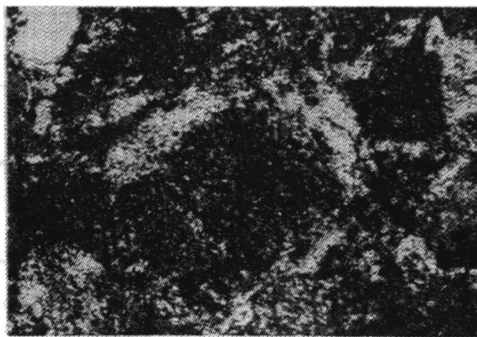


Fig. 3. Grain of glauconite surrounded by tangentially oriented films of mica minerals. The structure is typical of rocks that have undergone compaction in hydrostatic conditions (well 132, depth 2925 m, magnification 300).

usually interstitial, mixed in composition: ferruginous-argillaceous, sulfate-dolomitic, sulfate, and quartz. The transitional sulfate-terrigenous strata (Oskoba suite) are composed of unevenly interbanded terrigenous, clay, and thicker layers and members of carbonate and sulfate-carbonate rocks [24]. Formation of this lithological complex that is significantly similar to deposits of a contemporary sabkha (flat, periodically flooded, saline area) occurred in a very shallow-water basin with periodic drying of the sediments. The organic-matter content in the rocks varies in the range of 0.05-0.5%, up to 1.0-1.5% in layers of dark mudstones. Accumulations of black, carbonaceous material and increased bitumen content are frequently confined to the lower horizon of the Oskoba suite, which acts as a fluid barrier for gas and oil accumulations of the productive Vanavara suite. Bitumens are often confined to pockets of anhydrite.

The upper, carbonate part of the Vendian cross section in the composition of the Katanga, Soba, and Tetera suites is composed of interbanded dolomites, anhydrite-dolomites, and argillaceous dolomites with interlayers of clay-sulfate-dolomitic marls and mudstones with lenses of anhydrites and flints.

Mineralogical and Petrographic Characteristics of Terrigenous Deposits of the Ognev Series. Since it was precisely terrigenous rocks of the Ognev series that were used to substantiate the Rb-Sr age, they were studied in greater detail.

Rocks containing glauconite were formed by alternation of little layers of fine-grained feldspar-quartz sands, siltstones, and mudstones. The layers' thicknesses vary from millimeters up to 1-1.5 cm. In each petrographic variety of rocks forming a layered series, variable amounts of glauconite grains are present, which exceed the dimensions of clastic grains by many times. In individual sandy interlayers, glauconite becomes the dominant mineral. In siltstones and mudstones, it is only present in the form of an admixture.

Mudstones have a mixed composition and include a small amount of sedimentation-clastic admixture of flakes of muscovite, chlorite, and altered trioctahedral micas. The mudstones' black color and the abundance of very fine little crystals and aggregate grains of authigenic pyrite may indicate their original enrichment with organic matter. In siltstones, the admixture of organic matter and layered silicates is significantly smaller. Signs of postsedimentation compaction of siltstones are visible in the formation of films of clay minerals oriented in the same way around the periphery of each isometric grain, including grains of authigenic glauconite (Fig. 3).

The main authigenic epigenetic mineral of siltstones is anatase, which forms solitary little crystals, as well as concretions of very fine crystals grouped in the form of continuous masses or in the form of small aggregate clumps close together. Anatase crystals and aggregates are bordered by films of leucoxene. We can suppose a high degree of aggradation of micas, although in both mudstones and siltstones the greater part of the layered silicates has submicroscopic dimensions.

Interlayers of sandstones contain clastic quartz, rounded, as well as acute-angled. Among feldspars, orthoclase and microcline are dominant. Albite is noted in a small amount. Conformal articulation of fragments, overgrowth of quartz grains with authigenic fringes, regeneration of potash feldspars (Fig. 4a), and the appearance of little authigenic orthoclase crystals with no nucleus (see Fig. 4b) are seen everywhere. The primary pores are completely closed up. Idiomorphism

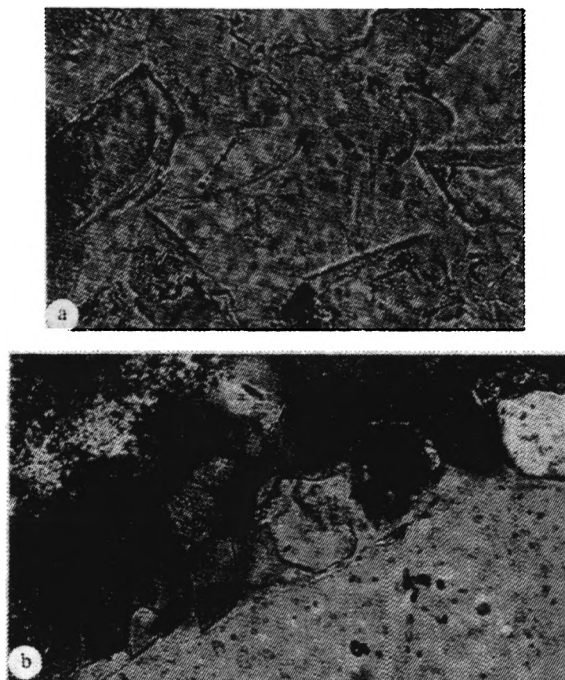


Fig. 4. Examples of formation of authigenic potash feldspars in sandstones of the Ognev series: a) rhomboidal authigenic crystals of orthoclase, with no nucleus in the right side of the photo, with a regeneration film of K-feldspar on a clastic grain in the left side; b) large clastic grain of quartz surrounded by a regeneration fringe. In the fringe of authigenic quartz, idiomorphic crystals of authigenic orthoclase with no nucleus are easily seen; authigenic regeneration quartz is xenomorphic (well 132, depth 2925 m, magnification 300).

of authigenic orthoclase is very clearly expressed, while authigenic quartz is xenomorphic (see Fig. 4a and b). Thus, formation of the contemporary mosaic structure and filling of the pore space occurred first as a result of formation of quartz and orthoclase, and subsequently residual voids were filled with quartz alone.

Glauconite grains preserve their globular form and are untexturized in all varieties of rocks of the layered series. Only in very fine sandy prisypki (crystal fragments on the top face of a larger crystal) between little layers of siltstones is glauconite crushed and spread out, as it were, in a little layer, forming extended texturized grains in which the arrangement of mica particles is subparallel to the layer.

In sands and siltstones, authigenic siderite is noted. It develops inside of glauconite globules, replacing them and the surrounding mass of clastic and authigenic silicate grains (Fig. 5). Thus, formation of siderite occurred in the latest stage, already after formation of the rock's mosaic structure.

Conformal articulation of grains in little sandy layers indicates that authigenic growth of quartz and feldspars began after the accumulation of fairly thick overlying strata of sediments. According to available estimates [16, 39, 54], occurrence of conformation of grains in sands and subsequent formation of mosaic structures require thicknesses of overlying layers of more than 1.5 km. Therefore, formation of authigenic orthoclase could have begun only after accumulation of at least 1.5-km strata of overlying rocks.

Considering the whole set of allo- and authigenic potassium-containing minerals, which are the most interesting in the context of the present article, we can note the following important peculiarities. The greater part of potassium- and, consequently, rubidium-containing minerals is represented by orthoclase and microcline. In the overwhelming majority of cases, they are authigenic, i.e., they were formed in the already existing rock in the stage of its epigenetic transformations. In large grains of potash feldspar, relict cores of clastic minerals are preserved. The greater part of micas also has an

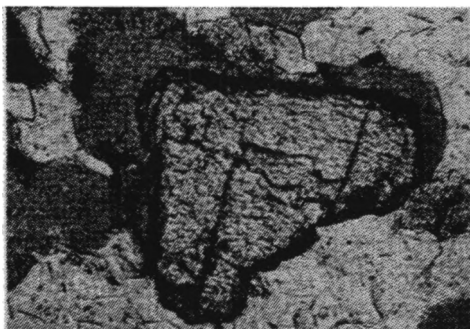


Fig. 5. Grain of siderite that has replaced a considerable part of a glauconite globule and part of the surrounding quartz and orthoclase grains (well 132, depth 2925 m, magnification 300).

authigenic nature. The amount of them is not great, and they usually also bear signs of degradation and subsequent aggradation. Microscopic observations show that the origination of neogenic potash feldspars is significantly separate in time from formation of glauconite, which, in turn, experienced partial or complete recrystallization and regeneration.

SAMPLING AND ANALYTIC EQUIPMENT

The location of the wells in which sampling was conducted is shown in Fig. 1; the lithological sections and intervals for each well, in Fig. 2. Samples for Rb—Sr determinations were taken in the form of small (thickness up to 1 cm) layer-by-layer chips.

Specimens weighing ~1 g were broken up to a size fraction of 1-2 mm and rinsed with water in an ultrasonic bath. The dried specimen was powdered, and a sample of about 200 mg was subjected to chemical treatment. From three specimens of glauconitic sandstone, pure fractions of glauconite (globules) were isolated first by magnetic separation, and then by hand. The nonmagnetic fractions of these specimens, consisting of grains of quartz and potash feldspar, were analyzed separately. Two specimens of fine siltstones with occasional grains of glauconite were treated for several hours by boiling 10 N HCl, and we analyzed the solution and the undissolved residue. With such treatment, decomposition of glauconite and, possibly, other clay minerals was supposed to occur, and clastic silicate particles would remain unaffected.

Determinations of the concentrations of Rb and Sr, and the isotopic composition of strontium were made by the method of isotopic dilution on an MAT-260 instrument according to the procedures described in [6, 8]. At present, a mixed tracer of ^{84}Sr — ^{87}Rb is used at the laboratory, with isotopic ratio ^{84}Sr — $^{86}\text{Sr} = 16.390$ and $^{85}\text{Rb}/^{87}\text{Rb} = 0.008316$, and concentrations of $[^{84}\text{Sr}] = 0.04376 \mu\text{g/g}$ and $[^{87}\text{Rb}] = 21.485 \mu\text{g/g}$. The tracer was added to samples of clay rocks before their decomposition, which was done with a mixture of HF and HNO_3 acids at room temperature for 24 h. Then, the samples were boiled down with perchloric acid and dissolved in 2 N hydrochloric acid. Separation of rubidium and strontium was done in chromatographic columns with inside diameter of 12-14 mm, extracted with 2.66 N hydrochloric acid. Then, the isolated fractions of rubidium and strontium were completely purified in small columns 4-6 mm in diameter with a resin volume of ~8 cm³. Strontium was extracted with 2 N HCl; and rubidium, with 0.6 N HCL. Samples of limestones, dolomites, and anhydrites were dissolved in 10% HCl, and the undissolved residue was weighed for calculation of concentrations in the dissolved part.

In the measurements, the isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ were normalized with respect to the amount of $^{86}\text{Sr}/^{86}\text{Sr}$, which was equal to 8.37521, and reduced to the value of $^{87}\text{Sr}/^{86}\text{Sr}$ equal to 0.70801 in the All-Russian Scientific Research Institute of Metrology's standard [7]. The isotopic ratio actually measured in the standard during work with this material was 0.70811 ± 1 for nine independent measurements. Measurement errors for the specimens, calculated from parallel tests over many years of work, are ~1% for $^{87}\text{Rb}/^{86}\text{Sr}$ and better than 0.00005 for $^{87}\text{Sr}/^{86}\text{Sr}$. Isochronous dependences were checked by the X^2 method [34]. Only when a measurement error of 1.5% is assigned for the amount of $^{87}\text{Rb}/^{88}\text{Sr}$ does the dependence change to isochronous. The errors given (2σ) were calculated according to D. York [78].

TABLE 1. Rb – Sr Characteristics of Upper-Precambrian Sulfate and Carbonate Rocks

Number			Depth, m	Suite	Rock	Rb, $\mu\text{g/g}$	Sr, $\mu\text{g/g}$	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
laboratory	field	well								
Vendian deposits										
3940	94	115	2430	Tetere	Anhydrite	1,62	82,4	0,057	0,71180	0,71069
3884	90	115	2450	*	Dolomite	0,67	291,0	0,0066	0,70815	0,70809
3939	85	115	2670	Oskoba	Anhydrite	0,13	943,2	0,0004	0,70892	0,70892
3938	82	115	2708	*	*	0,43	1222,0	0,001	0,70930	0,70930
3885	80	115	2710	*	Dolomite	1,12	586,3	0,0055	0,70897	0,70892
3924	79	115	2750	*	Anhydrite	0,35	632,4	0,0016	0,71076	0,71075
3922	78	115	2760	*	*	0,10	404,9	0,0007	0,71120	0,71119
3887	48	122	2576	Tetere	Dolomite	6,60	1558,0	0,0122	0,70817	0,70807
3920	42	122	2946	Oskoba	Anhydrite	0,19	527,0	0,0010	0,70800	0,70799
3933	39	122	3005	*	*	0,095	1003,0	0,0002	0,70867	0,70867
3994	37	122	3010	*	*	0,090	635,5	0,0004	0,70934	0,70934
3935	32	122	3033	*	*	0,106	378,0	0,0008	0,70940	0,70939
Pre Vendian deposits										
3881	28	131	2954	Kamov	*	0,364	35,5	0,0296	0,70631	0,70574
3943	21	131	2330	*	Dolomite	0,364	20,0	0,0526	0,70684	0,70557
3942	18	131	3430	*	*	0,36	26,8	0,039	0,70565	0,70487
3941	17	131	3506	*	*	0,155	32,4	0,0138	0,70568	0,70540
3918	12	131	3619	*	Anhydrite	0,101	776,0	0,0003	0,70439	0,70438
3914	7	131	3680	*	*	0,511	623,0	0,0023	0,70493	0,70488
3912	3	131	3707	*	*	17,34	768,0	0,0653	0,70684	0,70557

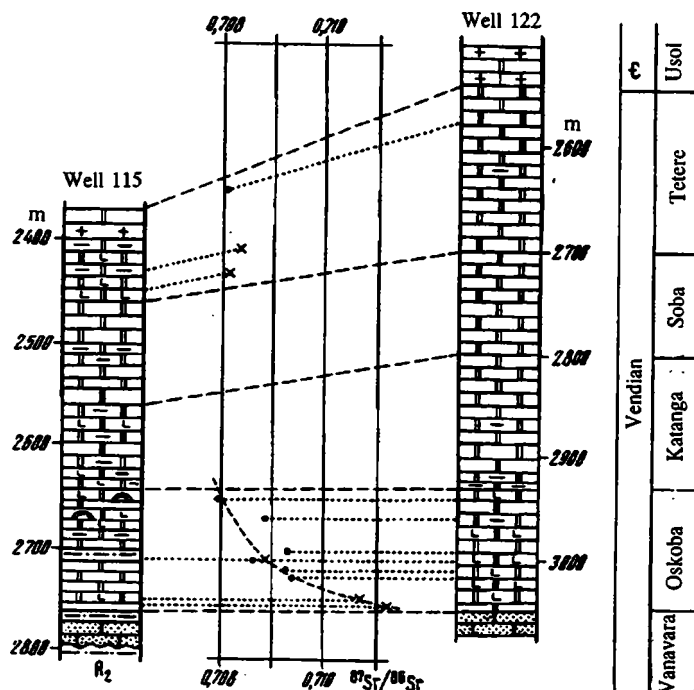


Fig. 6. Changes in isotopic composition of strontium in carbonate and sulfate rocks of the Vendian (wells 115 and 122). See Fig. 2 for conventional notations.

Decomposition of samples for isotopic analysis of carbon and oxygen was done with the help of H_3PO_4 in two stages: at 25°C (1 h) and at 100°C (1 h). Calcite was supposed to decompose in the first stage; and dolomite and magnesite, in the second one [68]. The amount of fractionation of oxygen isotopes as a result of decomposition of calcite, dolomite, and magnesite was taken as equal to 10.2‰. The values of $\delta^{13}\text{C}$ are given pro mille in relation to the PDB standard; $\delta^{18}\text{O}$, in relation to the SMOW standard. For referencing to PDB, we used the NBS-19 and KH-2 standards [56]. Values of $\delta^{18}\text{O}$ were converted in relation to SMOW according to the equation [52]

$$\delta^{18}\text{O}_{\text{SMOW}} = 1,03086_{\text{PDB}} + 30,86.$$

For isotopic analysis of sulfur, sulfates were dissolved in 10% HCl and then precipitated in the form of BaSO_4 . Decomposition of BaSO_4 was done with the help of V_2O_5 in the presence of copper at a temperature of 1100°C . Values of $\delta^{34}\text{S}$ are given pro mille in relation to the meteorite standard.

Measurements of the isotopic composition of carbon, oxygen, and sulfur were made on an MI-1201V mass spectrometer. The error in determining $\delta^{13}\text{C}$ does not exceed $\pm 0.1\text{‰}$; $\delta^{18}\text{O}$, $\pm 0.2\text{‰}$; and $\delta^{34}\text{S}$, $\pm 0.3\text{‰}$.

RESULTS AND DISCUSSION OF THEM

Strontium. Data on the isotopic composition of strontium in anhydrites and dolomites are given in Table 1 and in Figs. 6 and 7. The primary isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ have a large spread within the bounds of the suites for individual wells, as well as over the area. In Vendian deposits, the isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ vary in the range of 0.7080-0.7112; in Riphean deposits, 0.7044-0.7107. For wells 115 and 122 (see Fig. 6), within a 100-meter interval in the lower part of the Vendian cross section (Oskoba suite) we can see a regular increase in the isotopic ratio of strontium from 0.7081 to 0.7112. It would be easy to explain by a change in the isotopic composition of seawater in time. Such an explanation would seem the more likely as in the curve of evolution of the isotopic composition of strontium in seawater there are characteristic changes in the values of $^{87}\text{Sr}/^{86}\text{Sr}$ precisely in the middle of Vendian time (Fig. 8). We will pay attention,

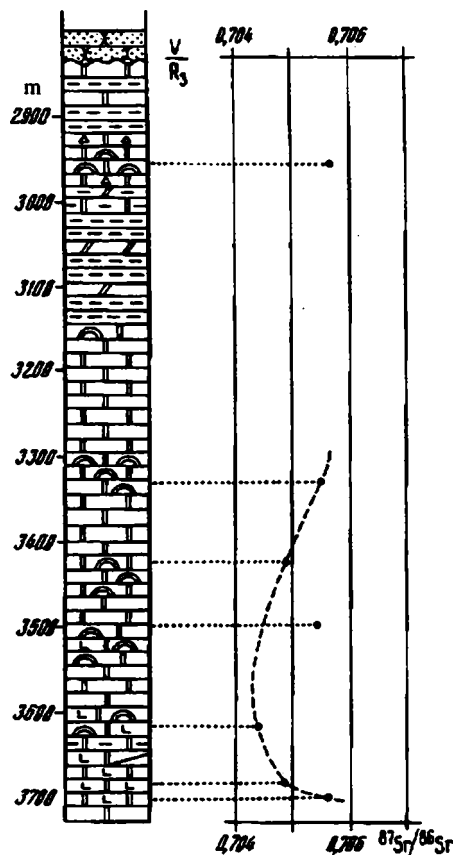


Fig. 7. Changes in isotopic composition of strontium in carbonate and sulfate rocks of the Kamov series of the Upper Riphean in the cross section of well 131. See Fig. 2 for conventional notations.

however, to the fact that the primarily sulfate-carbonate deposits of the Oskoba suite are underlain by terrigenous quartz-feldspar sandstones and mudstones, which, in turn, lie with erosion on terrigenous deposits of the Upper Riphean. The high contents of radiogenic strontium in terrigenous rocks may be a source of postsedimentation (epigenetic) contamination of sulfate-carbonate rocks of the Oskoba suite with radiogenic strontium.

Apparently, changes in the isotopic composition of strontium in sulfate-carbonate rocks of the Kamov series of the Upper Riphean in well 131 can be explained in just this way. There, the lowest values of $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.704$ come in the interval of 3500-3600 m (see Fig. 7). Up and down from this interval, the isotopic ratios of strontium rise to values of ~ 0.706 . The sulfate-carbonate strata of the Kamov series are replaced by carbonate-terrigenous strata upward through the cross section approximately from the level of 3510 m in well 131. Down through the cross section, approximately from the level of 3750 m, should be the roof of a primarily terrigenous series of the Middle Riphean. Thin interlayers of siltstones are already found near the bottom of well 131. The highest values of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7105 and 0.7107) are found closer to contacts with terrigenous strata and especially in thin interlayers of dolomites among terrigenous rocks of the basic series (see Table 1).

Thus, the isotopic composition of strontium in sulfate and carbonate rocks was subjected to epigenetic changes. In the Vendian part of the cross section, a 100-m interval of rocks was subjected to such changes; in the Kamov suite of the Riphean, a 500-m interval. This statement is in no way new. In constructing evolution curves of the isotopic composition of strontium in seawater in time, which we will discuss in greater detail below, the lower values of $^{87}\text{Sr}/^{86}\text{Sr}$ in carbonates of those measured are usually used, since contamination of rocks with radiogenic strontium is supposed to be likely. In the literature, there are specific examples that demonstrate the reality of this process. It has been shown, for example, that Jurassic carbonates in southwestern Arkansas (USA) were subjected to epigenetic recrystallization on account of brines which came into contact with terrigenous rocks in deeper parts of the cross section. As a result, the isotopic composition

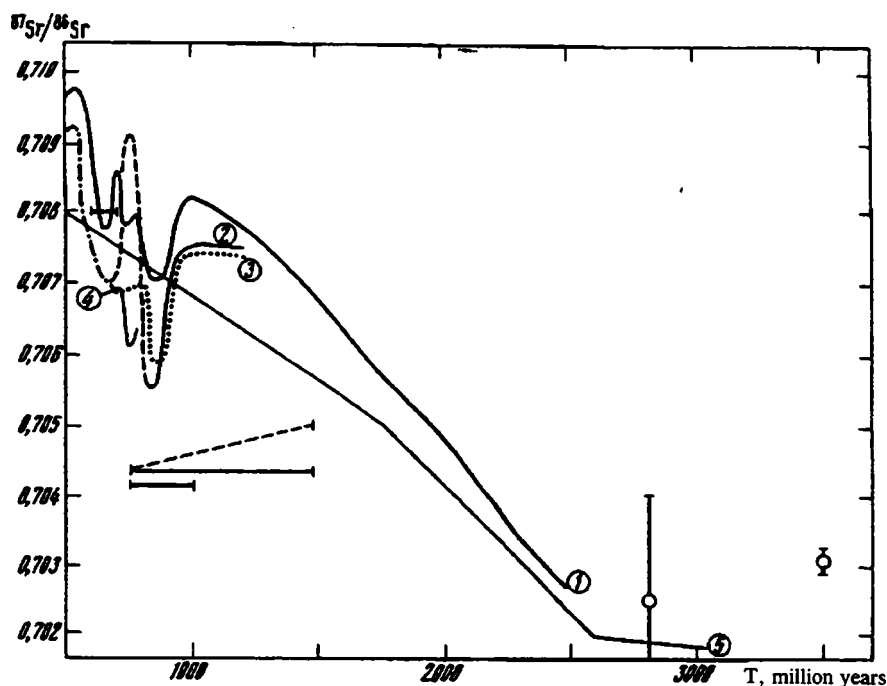


Fig. 8. Graphs of change in isotopic composition of strontium in seawater in the Precambrian. Curves are given according to data from: 1) [49]; 2) [72]; 3) [41]; 4) [47]; 5) [73]. The position of the points with age of 2.8 and 3.5 years is given according to [74]. The horizontal segments show the position of samples from deposits of the Kamov series and Vendian in the Katanga saddle; the sloped broken line, from the Kotuikan cross section according to data from [22]; and the horizontal solid line, the most likely isotopic composition of strontium in unaltered carbonates of the Katuikan cross section.

of strontium changed from 0.7068 for the primary carbonate material to 0.7096 for the recrystallized material [63, 76]. A clear example of epigenetic transformations of Devonian dolomites of the Western graywacke zone in the eastern Alps was demonstrated on the example of sheet deposits of barite [53]. The isotopic composition of strontium in the surrounding dolomites, in the barite, and in other epigenetic minerals was investigated over an area of 2×1.5 km and in a 600-m interval of dolomite strata.

Practically the whole volume of the inspected rocks had a mixed isotopic composition of strontium. The greatest number of values of $^{87}\text{Sr}/^{86}\text{Sr}$ lay in the range of 0.710-0.713, with a value of 0.708 for unaltered rocks [43]. Extensive investigations of the isotopic composition of strontium were conducted in Devonian dolomites in western Canada [64]. Early dolomites formed under the influence of Devonian seawater contain strontium with isotopic ratios of 0.7080-0.7083. Dolomites formed or transformed in the stage of epigenesis contain more radiogenic strontium, with isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ all the way up to 0.716. They include dolomites of the famous Paine Point deposit. Late dolomitization is supposed to be connected with Late-Cretaceous—Early-Tertiary time, in which the greatest subsidence of the region and probable rise of hot brines from deep parts of the cross section occurred. Contemporary formation brines in Paleozoic deposits of the region contain significantly radiogenic strontium with isotopic composition above 0.7095, in most cases, and all the way up to 0.7128. They get their radiogenic component from terrigenous rocks in lower parts of the cross section or from the basement complex [64].

Elemental ratios of Rb/Sr, Mn/Sr, and Ca/Sr, and also isotopic ratios of oxygen and carbon are often used to evaluate epigenetic changes in carbonate rocks and for taking the least altered samples for interpretation of strontium isotopic ratios [48, 55]. Correlations of these ratios with the isotopic composition of strontium are sometimes noted, which makes it possible to extrapolate them to the initial, least altered ratios.

We should emphasize once again that, in the overwhelming majority of cases, epigenetic changes in chemogenic (carbonate and sulfate) rocks lead to enrichment of strontium with the radiogenic isotope, i.e., to a rise in the isotopic ratio $^{87}\text{Sr}/^{86}\text{Sr}$. This is quite natural, since in cross sections of continental sedimentary rocks chemogenic sediments usually alternate with terrigenous and volcanogenic rocks with a "continental" appearance. Increased values of Rb/Sr in them lead

to surplus accumulation of radiogenic strontium in relation to chemogenic rocks. Consideration of possible mechanisms of its redistribution is beyond the interests of the present work. We will just say here that mechanisms of this sort do exist, and the rocks that we studied were subjected to serious material transformations, with redistribution of strontium between terrigenous and chemogenic components of the cross section. Nonetheless, it is possible, it seems to us, to establish the isotopic composition of strontium in the original, unaltered rocks, or to come close to it and thus determine the isotopic composition of strontium in seas of that time.

Evolution of the Isotopic Composition of Strontium in Waters of the World Ocean. In the waters of contemporary oceans and seas, the isotopic ratio of strontium is constant: 0.7092. This constancy is determined by the rather long time that strontium stays in seawater. It is about 10^8 years, which exceeds by three orders the time for mixing of oceanic waters [69]. Oceanic reservoirs are fed with strontium on account of two categories of rocks that are fundamentally different in the isotopic composition of this element: rocks of the continental and oceanic crust. Rocks of the continental crust are characterized by high and very different isotopic ratios of strontium. Its average composition is determined by river flow, but in rivers, depending on what regions they drain, the isotopic composition of strontium varies in a wide range (0.7045–0.950). However, the main large rivers carry strontium with ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7095 to 0.7123, and the mean value of this ratio in river flow is 0.7119 [57, 65, 71]. The main source of strontium in continental runoff is carbonate rocks and evaporites.

Of rocks of the oceanic crust, the main carriers of strontium are basalts with an average isotopic ratio of $^{87}\text{Sr}/^{86}\text{Sr} = 0.703$; they have been altered only slightly in the direction of an increase during the Earth's whole geological history, in connection with the low value of Rb/Sr in basalts. Consequently, ~75% of the strontium in the contemporary oceans comes with river flow, and only approximately 25% from basalts of the ocean bottom. Thus, the isotopic composition of strontium in seawater serves as an important geochemical indicator of the planet's geological activity, and that is why it is so important to trace its evolution in time.

This can be done according to chemogenic sedimentary rocks, which were deposited in equilibrium with seawater and inherited the isotopic composition of strontium in the sedimentation basin. Such rocks include, first of all, carbonates, sulfates, and phosphates, which contain high amounts of strontium and, consequently, possess buffer properties in relation to preservation of the strontium system. Nonetheless, as was shown above, as a result of postsedimentation changes in the rocks, displacements of the isotopic ratios are possible, which has to be taken into account in interpreting the data. Another complication in constructing global curves of the evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in time is connected with difficulties in age correlation of the rocks being studied. Naturally, they are less for the Phanerozoic, especially Mesozoic deposits, and detailed works have been conducted for this time interval [50, 58, 59, 61]. It has been shown that the peaks of maximum values of $^{87}\text{Sr}/^{86}\text{Sr}$ correspond to times of increased tectonic activity and, as a consequence, to intensification of the erosion of continental blocks. A very indicative example is the rise in value of $^{87}\text{Sr}/^{86}\text{Sr}$ in the last 40 million years: from 0.7075 to 0.7092, which is connected with the collision of the Indostan and Asiatic continents and the uplift of Tibet and the Himalayas [67].

Naturally, it is impossible to achieve such detail for Precambrian deposits. Figure 8 shows various authors constructions, beginning from one of J. Veizer and W. Compston's first works, published in 1976 [73], and ending with works of recent years. We can see the fundamental similarity of these curves, although differences in the details are fairly large. Our attention is drawn to the complexity of the curves in the interval of 0.5–1 billion years and their relative monotony for more ancient time intervals. This is connected, of course, primarily with limitations in the detailedness of sampling, and with time all of the curves will acquire the same complex nature. Unfortunately, the questions remains, does this complexity reflect actual variations in the isotopic composition of strontium in seawater of that time or is it a consequence of epigenetic, postsedimentation transformations of the rocks. The presently suggested criteria do not make it possible to get a definite answer [72]. At best, it is possible to throw out specimens known to be altered or to be cautious about the results. In our case, the selection of thick strata of chemogenic rocks for the investigation and checking of the effect of terrigenous rocks on the isotopic composition of strontium in them enabled us to evaluate the composition of strontium in the original rocks with a high degree of probability.

The results of this evaluation are shown in Fig. 8. The value that we derived, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$, for Vendian time agrees, in general, with previously known data, although it does not confirm the presence of a negative peak, which comes precisely in Vendian time on the evolution curves (see Fig. 8). Perhaps this is connected with incompleteness of the cross section of Vendian deposits in Siberia. This discrepancy does not seem to be fundamental, although it does, of

TABLE 2. Isotopic Ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ and Concentrations of Rb and Sr in Rocks of the Katanga Saddle

Number		Depth, m	Characteristics of the specimen	Rb, μg/g	Sr, μg/g	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr
labora- tory	well						
Oskoba suite, Vendian							
3880	115	2670	Mudstone	96,5	66,15	4,233	0,73534
Ognev suite							
4017	107	2960	Glauconite from sandstone	266,6	25,42	32,05	1,28183
4019	132	2928	"	330,0	20,18	51,77	1,66890
4022	132	2925	"	306,3	55,64	16,42	1,02223
4004	132	2925	Glauconitic sandstone, HCl extract	255,5	121,0	6,178	0,82673
4005	132	2925	"	471,2	153,4	9,040	0,88132
3872	132	2925	Siltstone	288,2	287,1	2,923	0,77165
3876	132	2925	"	290,0	280,7	3,009	0,77177
3877	132	2920	Mudstone	219,8	179,8	3,563	0,78317
4016	132	2925	"	238,3	177,6	3,913	0,79369
3875	132	2925	Siltstone	145,6	76,51	5,239	0,82018
2878	115	3160	Mudstone	167,0	109,0	4,474	0,80606
4006	132	2925	Sandstone, residue after dissolution	282,0	350,7	2,340	0,76797
4005	132	2925	HCl extract from sandstone (4006)	212,1	226,8	2,723	0,77238
4020	132	2928	Glauconitic sandstone, nonmagnetic fraction (glauconite 4019)	104,2	87,05	3,496	0,80146
4023	132	2925	Glauconitic sandstone, residue from dissolution in HCl (4005)	154,1	36,11	4,378	0,81170
4003	132	2925	The same (4004)	90,94	60,40	4,401	0,81351
4018	107	2960	Glauconitic sandstone, nonmagnetic fraction (glauconite 4017)	109,3	89,94	3,589	0,79662

course, require further verification. Data on Riphean deposits are radically at odds with the evolution curves, and this is true of deposits of the Katanga saddle, as well as previously studied deposits of the western slope of the Anabar shield [22].

In Fig. 8, the broken line is drawn according to actual measurements. Its slope is connected with a gradual rise in values of $^{87}\text{Sr}/^{86}\text{Sr}$ down through the cross section from 0.704 in the Yusmastakh suite of the Upper Riphean to 0.705 in the Ust'-Ilya suite of the Lower Riphean. At present, relying on the data discussed here for the Katanga Saddle, we are inclined to attribute this rise in isotopic ratios of strontium to the effect of terrigenous rocks lying in the lower part of the cross section. Therefore, the most likely, it seems to us, isotopic ratio of strontium in carbonates of the Kotuikan cross section is shown by the solid horizontal line. In any case, the data that we obtained lie on the graph (see Fig. 5) significantly below the evolution curves.

We can suggest three possible reasons for such a discrepancy. First of all, this may be a consequence of provincial peculiarities of the cross sections that we studied. The likelihood of such an explanation seems very low. The two cross sections (Kotuikan and Vanavara) are separated from each other by 1000 km. The Kotuikan cross section is considered one of the reference cross sections for the Riphean of the Siberian craton [30]. Secondly, the discrepancy under consideration may be a consequence of imperfection of our knowledge about evolution of the isotopic composition of strontium in seawater in time, and the evolution curves have to be fundamentally corrected. Such a hypothesis also seems unlikely. This is primarily true of the time interval of the Upper Riphean, for which practically all of the world's representative cross sections have been studied, and their position on the time scale is the most definite among Precambrian formations. Therefore, new data on the Upper Riphean can only refine the established pattern, but not change it fundamentally. There remains, finally, a third hypothesis. It is that the stratigraphic position of the cross sections that we studied does not

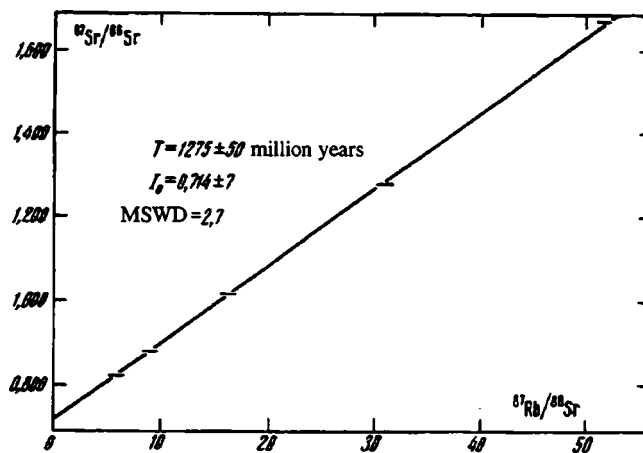


Fig. 9. Rb – Sr diagram for glauconites from deposits of the Ognev series of the Katanga saddle and hydrochloric-acid extracts from glauconite-containing rocks. The length of the dashes on the graph corresponds to 1.5% error in measurements of the amounts of $^{87}\text{Rb}/^{86}\text{Sr}$. The thickness of the dashes exceeds the analytic error in the amount of $^{87}\text{Sr}/^{86}\text{Sr}$. MSWD – mean square of weighted deviations.

correspond to the accepted one, and the so-called Upper- and Middle-Riphean deposits are in fact Lower-Riphean or even older. Such a hypothesis has already been expressed previously for the Kotuikan cross section [22] and is now confirmed on the Vanavara cross section. What is more, the attempt to determine the Rb–Sr age of "Riphean" deposits of the Katanga saddle also leads to a conclusion about its nonconformity to the accepted stratigraphic division.

Rb–Sr Dating. The results of Rb–Sr measurements are given in Table 2 and in Figs 9 and 10. From Vendian deposits, only one determination was made, according to the overall sample of mudstone. Model calculation for an initial isotopic ratio of strontium of 0.708 give an understated age (460 million years). It hardly makes sense to discuss this isolated result. We will only note that understatement of the isotopic age of clay rocks is a frequent phenomenon and is usually linked with secondary transformations of them.

In preVendian deposits, the basic material was taken from a core segment ~ 10 cm high from a depth of 2925 m in well 132. The rock is a thin alternation of little layers of sandstones with and without glauconite, siltstones, and black phyllite-like shales. From three specimens, we took pure globules of glauconite; two glauconite-containing specimens were treated with strong hydrochloric acid, and the acid extracts were analyzed. All five of these specimens form an isochronous dependence (see Fig. 9), which corresponds to an age of 1275 million years and an initial value of 0.714. The large error of the initial ratio is explained by the points' considerable spread around the straight line and the absence of points with low values of Rb/Sr. A valid objection can be raised to the use of acid dissolution, which can affect other mineral components of the rock. However, as we can see from the position of the points on the straight line in Fig. 9, the main dissolved component was glauconite or other clay minerals paragenetic with it, and the probable terrigenous component was practically unaffected. Elimination of these two points from the calculation practically does not change the slope of the isochrone. The age value obtained according to glauconites corresponds to the Middle Riphean and is close to available results of K–Ar dating of glauconites.

Another series of measurements was made on overall samples of fine-grained rocks, which were arbitrarily separated according to macro- and microscopic traits into siltstones and mudstones. Their overall petrographic characteristics were given above. Five of these samples were taken from various little layers of a 10-cm piece of the core from well 132, and a sixth one was also taken from the Ognev series in well 115. The distance between these two wells is ~ 300 km. All six samples form an isochronous dependence with age of 1526 million years and an initial ratio of 0.7067 (see Fig. 10).

World experience in working on dating of sedimentary rocks, which has been generalized, in particular, in [10, 16, 28, 45, 46], shows that clay fractions, and silt ones even more so, can contain a terrigenous component, which either disrupts or gives a false isochronous dependence. Various methods are used to check this danger. Usually, size fractions

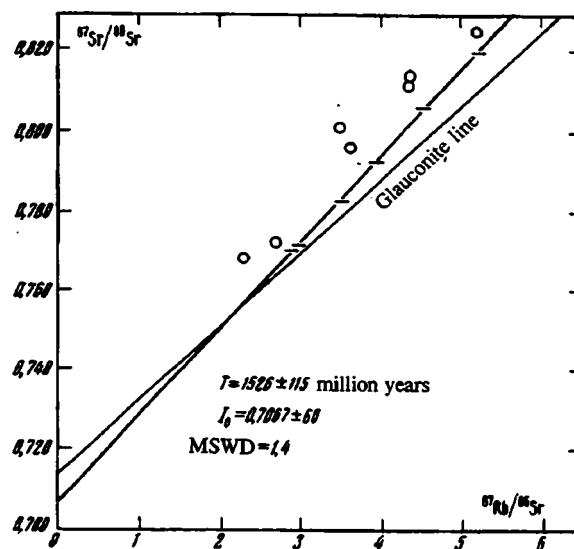


Fig. 10. Rb—Sr diagram for fine-grained clastic rocks of the Ognev series. The isochrone for glauconites is shown for comparison; circles indicate the results of measurements of the quartz-microcline fraction from the same rocks. The length of the dashes corresponds to 1.5% error in measurement of $^{87}\text{Rb}/^{86}\text{Sr}$; the thickness of the dashes exceeds the analytic error in amounts of $^{87}\text{Sr}/^{86}\text{Sr}$; MSWD — mean square of weighted deviations.

of clay particles are isolated, and structural, mineralogical, and other types of analysis of them is carried out. In doing so, it is often forgotten that such works are primarily necessary to prove the minerals' authigenicity, since the very location of points on a straight line in isochronous coordinates is a phenomenon so strictly determined that the age meaning of a rectilinear dependence can seldom raise any doubt. It is obvious that, in our case, the derived age does not reflect the stage of diagenesis, but records some time of the rocks' epigenetic transformations, for example, the time of formation of secondary potash feldspars and mica minerals so characteristic of them.

This is confirmed by analysis of a third group of samples (see Table 2) of sandy size. Part of them is the nonmagnetic fraction of glauconitic sandstones, which consists of grains of quartz and feldspar. Two samples are residues from dissolution in strong hydrochloric acid; one is a hydrochloric-acid extract. All of these samples lie above the isochrone for fine-grained rocks (see Fig. 10) and, naturally, do not form a rectilinear dependence. Formal calculation of age according to the whole set of them gives a value of ~ 1600 million years. As we already said above, grains of potash feldspars in the coarse-grained fraction are not completely replaced by neogenic K-feldspar and have preserved cores of the original clastic component. The most likely source of removal of terrigenous sediments was metamorphic rocks of the craton's basement complex analogous to those that crop out on the Aldan and Anabar shields. They have different ages, but the most often found isotopic age of basement rocks is close to 2 billion years [9, 13, 21, 40], and this is precisely the age that should be recorded by clastic particles. Epigenetic transformation disrupted the Rb—Sr system even in the coarse fraction of terrigenous rocks, but not so much as to set the radioactive clock back to zero, which explains the position of the points in Fig. 10. Similar examples from published data were summarized in [10].

The isochrone that we derived for overall samples of fine-grained rocks can raise the greatest doubts. In such cases, researchers frequently resort to a seemingly simple explanation of the rectilinear dependence as a mixing line. One has to consider, however, that a rectilinear dependence in isochronous coordinates is obtained as a result of mixing of two components lying above and below the actual points on the approximating line. In our case, the most likely components of mixing could be clay minerals, on the one hand, and clastic potash feldspars, on the other. But a glance at Figs. 9 and 10 is sufficient to see that such components do not exist with the recorded values of Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$. Both clay minerals and potash feldspars display a very wide range of these ratios, and it is unlikely that their random natural combination would give a rectilinear dependence within the framework of a mixing model. We have to conclude that the rocks that

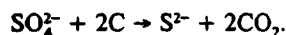
we studied underwent several stages of secondary transformation. One of them was recorded by Rb—Sr systems in glauconites we and corresponds to a Middle-Riphean age. Another one in the same rocks was recorded by Rb—Sr systems of fine-grained deposits. It corresponds to a Lower-Riphean age.* Accordingly, the age of sedimentary strata turns out to be Lower-Riphean or pre-Riphean. Their lower age limit is bounded, in all likelihood, by the time of the last stage of metamorphism of rocks of the craton's basement complex, i.e., approximately 2000 million years. This is precisely the age that agrees well with the isotopic ratios of strontium considered above.

An isochrone with age of ~1500 million years was obtained according to glauconites from the Ust'-Ilya suite of the Lower Riphean of the Kotuikan cross section, and its authors [11] interpret its value as the age of sedimentation or early diagenesis. It seems to us that among the arguments that they considered in favor of such an interpretation the decisive one was their persuasion that the derived age corresponds to the rocks' stratigraphic position. Our data show that rocks in both the Kotuikan and Vanavara cross sections are in fact close stratigraphic analogs, but make us doubt the validity of the stratigraphic position accepted for them. In connection with this, we should note that there are contradictions between the traditional schemes of stratigraphic subdivision in the territory of Siberia and new micropaleontological data. In the opinion of A. F. Veis and N. G. Vorob'eva, who studied organic-walled microfossils, the Kotuikan cross section may not contain sharp age boundaries and could be completely classified in the Upper Riphean, i.e., it could correspond to the age accepted for the Kamov series of the Katanga saddle. An Upper-Riphean age of the Kotuikan cross section follows from microbiota found in it that are similar to microbiota of Upper-Riphean deposits in the Urals and the Uchur-Mai region, the stratotype and hypostratotype of the Riphean [30]. At the same time, the similarity of Anabar microfossils to microfossils of the Roper series (Northern Australia), the minimum age of which is estimated as 1430 million years [66], is pointed out in [3].

Sulfur. The isotopic composition of sulfur in anhydrites was studied in the cross section of three wells (Table 3). In wells 115 and 122, we sampled Vendian deposits; and in well 131, the lower part of the Kamov series. All of the samples are distinguished by heavier isotopic composition in relation to contemporary oceanic sulfate and contain $\delta^{34}\text{S}$ from +29 to +39‰, although the time break between deposits of Vendian rocks and the Kamov series reaches 10^9 years.

The very fact of finding evaporites at a relatively ancient time level is interesting here. The generation of researchers active today still remembers when it was thought that deposits of evaporites did not occur in the Precambrian. Meanwhile, evidence of the former existence of evaporites in the Precambrian has been given [4, 5, 32, 33, 44]. The absence of direct finds of evaporites was due to their instability and removal from cross sections in the course of secondary transformations of the rocks. At present, these arguments belong to history, and there is already no doubt about the former salinity of the Precambrian. Nonetheless, each direct find of ancient evaporites expands our information about their extent and about sedimentation conditions, especially on the basis of study of the isotopic composition of sulfur.

The most unstable part of the evaporite cross section is chloride layers. They are squeezed out of the cross section, readily dissolved, and subjected to chemical decomposition at increased temperatures. Therefore, direct finds of halite in Precambrian sedimentary and metamorphic rocks are practically unknown. Sulfates are more stable in their physical properties, but are easily subjected to chemical decomposition. In contact with organic matter and other reducing agents, they decompose, forming hydrogen sulfide and carbon dioxide according to the scheme



At low temperatures, bacterial reduction of sulfates takes place; at high temperatures, abiogenic reduction.

All large accumulations of hydrogen-sulfide gases in the Earth's sedimentary mantle were formed as a result of reduction of sulfates. This process has global geochemical significance, and one has to be surprised that direct finds of anhydrites are still uncovered in ancient deposits, even in oil- and gas-bearing regions.

As a result of reduction of sulfates, primarily the light isotope of sulfur passes into hydrogen sulfide, and its heavy isotope gradually accumulates in the sulfate residue. The more sulfate is reduced, the heavier the sulfur in the sulfate residue will be.

*According to the latest summary [31], the Upper, Middle, and Lower Riphean encompass time intervals of 650-1000, 1000-1350, and 1350-1650 million years, respectively.

TABLE 3. Isotopic Composition of Sulfur in Upper-Precambrian Anhydrites of the Katanga Saddle

Number		Depth, m	Suite	$\delta^{34}\text{S}$
Specimen	Well			
94	115	2430	Tetere	35,3
91	115	2440	"	33,5
90	115	2450	"	34,8
89	115	2558	Katanga	35,7
85	115	2640	Oskoba	34,9
81	115	2705	"	32,9
82	115	2708	"	32,8
80	115	2710	"	33,6
79	115	2750	"	33,4
78	115	2760	Vanavara	28,8
43	122	2868	Katanga	35,7
42	122	2945	Oskoba	38,8
41	122	2949	"	34,6
40	122	2956	"	35,7
39	122	3005	"	34,0
37	122	3010	"	32,5
30	122	3035	"	30,7
32	122	3037	"	30,9
20	131	3360	Kamov	35,5
15	131	3594	"	37,0
12	131	3619	"	31,0
11	131	3619	"	32,5
98	131	3664	"	29,1
89	131	3664	"	30,9
7	131	3680	"	31,7
4	131	3696	"	28,7
3	131	3707	"	29,2

Previously, one of the authors of this article tried more than once to show that the heavier isotopic composition of sulfur in Cambrian evaporites is connected with secondary processes of sulfate reduction, and not inherited from the time of sedimentation. The original value of $\delta^{34}\text{S}$ of Cambrian evaporites and marine sulfate in Cambrian time was apparently close to the contemporary one (+20‰) [5, 65, 77]. It has not been ruled out that the high values of $\delta^{34}\text{S}$ found in Vendian (well 115) and preVendian (well 131) deposits of the Siberian craton are also connected with such a process. If one considers that the original values of $\delta^{34}\text{S}$ for Precambrian anhydrites were close to +20‰, then an increase to 35‰ on the average would mean that at least half of the original amount of sulfates in the cross section had been destroyed by reduction. This portion rises even more if we adopt lower original values of the anhydrites' $\delta^{34}\text{S}$.

The sole example known to the authors of reliable evaporite deposits of the Upper Precambrian in which the isotopic composition of sulfur has been studied is the Grenville series in Canada. The age of the deposits is estimated as 1200 million years. The values of $\delta^{34}\text{S}$ for sheet anhydrites of the Grenville series lies in the range of 14.5-26.1, with a mean value of +20 [42]. The large spread and the presence of fairly low values of $\delta^{34}\text{S}$ show that the sulfates in these rocks were less affected by epigenetic reworking than sulfates of the Katanga series in Siberia. Therefore, sections with isotopic ratios of sulfur close to the original ones were apparently preserved in them.

For every one molecule of hydrogen sulfide that is formed in reduction of sulfate, two molecules of CO_2 are produced, as a result of oxidation of organic carbon by the sulfate's oxygen. This carbon is distinguished by low values of $\delta^{13}\text{C}$ (about -25‰), and in the case of its interaction with carbonate carbon ($\delta^{13}\text{C} \approx 0$) the latter can be enriched with light carbon. It would seem that in the vicinity of zones of sulfate reduction carbonate rocks should be recrystallized under the influence of carbon dioxide that is generated and change their isotopic composition. In fact, this often happens in contemporary or young zones of sulfate reduction, of which deposits of native sulfur serve as a good example. However, in rocks of the preVendian member of well 131 no sign of a shift in the isotopic composition of carbon in surrounding carbonates is noted (Table 4). Two explanations of this fact are possible. The first one is that this is precisely the isotopic composition of sulfur that was characteristic of the sedimentation basin. The second one (which seems more likely to the

TABLE 4. Isotopic Composition of Carbon and Oxygen in Upper-Precambrian Carbonates of the Katanga Trough

Number		Depth, m	Suite	Rock	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Specimen	Well					
68	107	2790	Ognev	Dolomite	1,1	19,8
70	107	3100	"	"	1,2	24,0
94	115	2430	Tetere	"	0,9	25,5
90	115	2450	"	"	-1,4	25,1
86	115	2569	Katanga	"	-3,2	25,5
84	115	2702	Oskoba	"	-4,5	25,0
81	115	2705	"	"	-9,3	25,8
80	115	2710	"	"	-9,0	24,9
78	115	2760	Vanacara	"	-2,6	26,1
76	115	3095	Ognev	"	-1,4	25,0
75	115	3140	"	"	-1,3	23,8
96	122	2476	Usol	Limestone	1,2	21,5
48	122	2576	Tetere	Dolomite	0,7	25,8
44	122	2863	Katanga	"	-6,3	24,6
42	122	2945	Oskoba	"	-5,5	22,3
41	122	2949	"	"	-8,1	25,7
38	122	3010	"	"	-2,1	27,2
35	122	3021	"	Magnesite	-1,3	27,6
34	122	3028	"	"	-1,0	26,9
31	122	3034	"	"	-1,0	28,6
49	132	2225	Soba	Dolomite	-0,2	25,0
50	132	2232	"	"	0,1	25,5
51	132	2240	"	"	0,5	25,4
52	132	2245	"	"	-1,6	25,7
53	132	2253	"	"	-2,3	24,9
54	132	2470	Oskoba	"	-1,5	23,6
56	132	2650	Kamov	"	0,6	26,1
61	132	2812	Ognev	"	0,1	24,7
64	132	3000	"	"	0,7	24,3
28	131	2954	Kamov	"	1,2	26,0
21	131	3330	"	"	1,6	27,8
20	131	3360	"	"	1,4	24,1
18	131	3430	"	"	1,4	23,8
17	131	3506	"	"	-0,7	25,5
14	131	3596	"	"	1,6	26,5
4	131	3696	"	"	1,3	26,4

authors) is that in the course of subsequent epigenetic transformations the isotopic composition of carbon in carbonate rocks was averaged out, and the overall isotopic effect was completely obliterated. The ratios of stable isotopes in the Vendian part of the cross section are discussed in a special section.

Carbon and Oxygen. Data on the isotopic composition of carbon and oxygen in carbonate rocks are given in Table 4. The isotopic composition of oxygen in carbonates is fairly homogeneous in all of the sampled wells and intervals and is in the range of $25 \pm 2\%$ in most cases, which is typical of normal sedimentary carbonates. The isotopic composition of carbon in carbonates of preVendian deposits is also very homogeneous. The values of $\delta^{13}\text{C}$ usually do not go beyond the bounds of $0-2\%$, which also corresponds to the isotopic composition of carbon in sedimentary carbonates. These data seemingly contradict the results discussed above, which indicate powerful epigenetic reworking of the rocks. One has to recognize that the oxygen and carbon systems in carbonates are more conservative in secondary reworking of rocks than is the strontium system. A similarly strong expression of the isotopic effects of strontium in comparison with carbon and oxygen has been demonstrated on the example of a number of cross sections of Upper-Precambrian deposits [49] and in Early-Paleozoic dolomites of the eastern Alps [53].

This circumstance opens the fundamental possibility of using isotopic data on oxygen and carbon for clarifying the conditions of sedimentation and correlating cross sections, on which many researchers have recently been working enthusiastically.

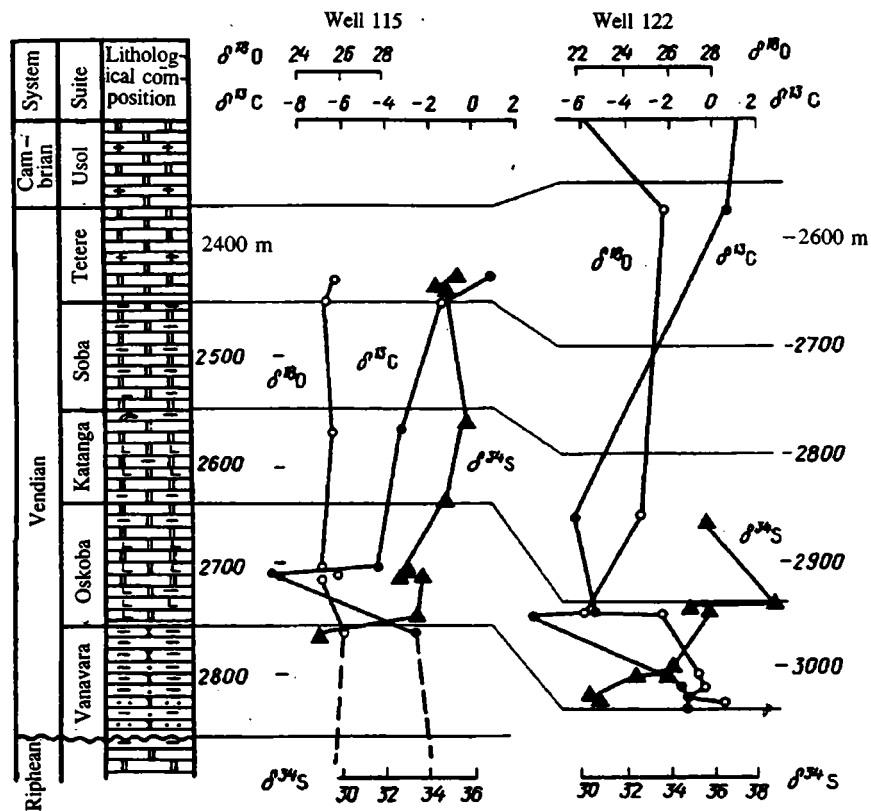


Fig. 11. Variations in the isotopic composition of carbon and oxygen in carbonates, and of sulfur in anhydrites in Vendian-Lower-Cambrian deposits of the Katanga saddle. See Fig. 2 for conventional notations.

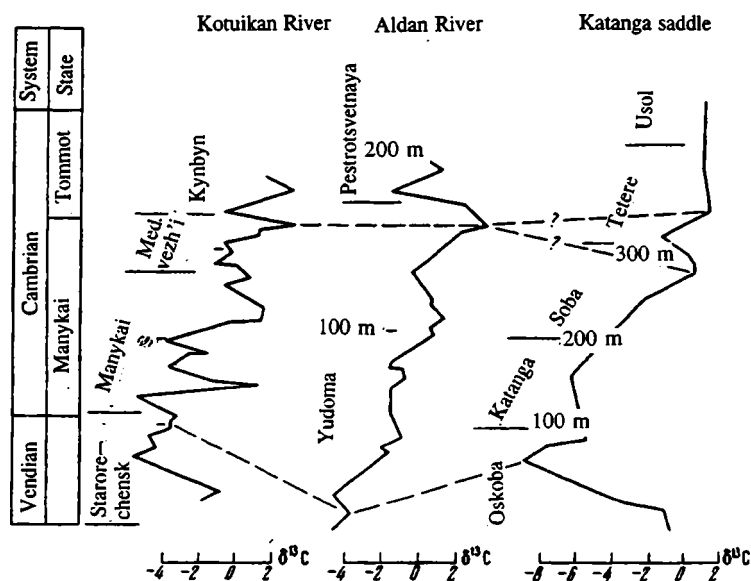


Fig. 12. Correlation of curves of change in isotopic composition of carbon in Vendian-Lower-Cambrian cross sections of the Western Anabar region [23], the Aldan River [61], and the Katanga saddle. The scheme of stratigraphic subdivision of transitional strata is given according to [20].

Vendian Anomaly in the Isotopic Composition of Carbon. The uniform distribution of values of $\delta^{13}\text{C}$ in Upper-Precambrian deposits of the Katanga saddle has one exception. It is in carbonates of the Oskoba suite, which were sampled in wells 115 and 122 (Table 4). In the cross sections of both wells, in the upper part of the Vanavara and lower part of the Oskoba suites the amounts of $\delta^{13}\text{C}$ are close to zero, i.e., they correspond to "normal" conditions of formation of carbonates. In the upper part of the Oskoba suite, a sharp peak of negative values of $\delta^{13}\text{C}$ is observed, all the way to -9.3 . Further up through the cross section, within the bounds of the Katanga and Soba suites, they once again approach normal and remain so all the way to the Usol suite of the Lower Cambrian.

An isotopic carbon anomaly in Vendian time is noted in the Siberian craton, eastern Greenland, and on Spitsbergen Island [23, 60, 62], and it apparently has global significance. In Tables 3 and 4 and in Fig. 11, we can see an inverse relationship in changes in the isotopic composition of carbon and sulfur in sulfate-carbonate deposits of the Oskoba suite. This circumstance may be of decisive significance for understanding the nature of the isotopic carbon anomaly. As was already discussed above, the heavier isotopic composition of sulfate sulfur may be connected with processes of sulfate reduction, which lead to release of corresponding amounts of carbon dioxide enriched with the light carbon isotope. Upper-Vendian—Lower-Cambrian time was characterized by a buildup of evaporite that is unusual in the Earth's history [14]. Apparently, large accumulations of organic matter arose during this period of geological history [51, 70]. All of this could lead, still in the sedimentation stage or later, to an upsurge of processes of sulfate reduction and release of enormous amounts of light carbon dioxide, a product of oxidation of organic matter. This process could, in turn, lead to a rise in the concentration of carbon dioxide in the atmosphere and, as a consequence, to serious ecological rearrangements.

Characteristic changes in the isotopic composition of carbon at the boundary of the Cambrian and Precambrian can be used for interregional stratigraphic correlations. In Fig. 12, data for the Katanga saddle are correlated with other cross sections of the Siberian craton: Kotuikan [22, 23] and Aldan [62], which are 1000 and 1500 km away from the Katanga cross section to the north and southeast, respectively. Of course, exact correlation of such remote cross sections is difficult. It is believed [37] that the upper part of the Soba suite of the Katanga saddle correlates with the Yuryakh subhorizon of inner regions of Siberia. Isotopic data agree with this hypothesis. With respect to negative anomalies of $\delta^{13}\text{C}$, the Oskoba suite of the Katanga cross section can be correlated with the Starorechensk suite of the west slope of the Anabar uplift and, possibly, with the lower part of the Yudoma suite in the "Dvortsy" cross section on the Aldan River.

The upper part of the Soba and lower part of the Tetera suites — the level at which relatively stable, "normal," i.e., close to zero, values of $\delta^{13}\text{C}$ are observed — can be correlated with the upper part of the Manykai and the Medvezh'i suite in the Kotuikan cross section, and with the upper third of the Yudoma suite in the Aldan cross section. The lower boundary of the Tommot stage, which is marked in the Kotuikan and Aldan cross sections by a positive isotopic anomaly, is not distinguished by core material in the Katanga saddle.

As is known, there are serious differences of opinion in determining the lower boundary of the Cambrian between various researchers, which have found reflection in Figs. 11 and 12. According to the scheme approved by the ISG [27], the boundary between the Vendian and Cambrian runs along the foot of the Tommot stage, as is shown in Fig. 11. The scheme in Fig. 12 uses V. V. Missarzhevskii's scheme, which is correct in our view and suggests including one more stage as part of the Lower Cambrian, the Manykai, which is characterized by the most ancient set of skeletal fossils [20]. In the northern part of the Siberian craton, where typical cross sections of the Manykai stage are located, the appearance of the first skeletal fossils practically coincides with the negative isotopic carbon anomaly [23].

* * *

Consideration of the data raises several fundamentally important questions. The first of these relates to the age of "Riphean" deposits of the Katanga saddle and, possibly, even of the whole Siberian craton. We can definitely say that, at present, this age has not been established by isotopic methods. At best, we can talk about a minimum age limit, i.e., about the time of significant metamorphic or epigenetic changes in the rocks. It is well known that isotopic dating of ancient sedimentary rocks is an extremely complex business, laborious and unreliable. This is connected with two main circumstances. First, there is always the danger of contamination of the clay minerals being dated with a terrigenous admixture, as a consequence of which dates that are too old can be obtained. Secondly, the rocks being dated may have been altered by secondary, epigenetic processes, which usually leads to understated age values. Finally, the action of the two factors together may simply make it impossible to obtain age information. Special techniques have been developed for preliminary

processing of the material to be analyzed [11, 29, 44, 45], but in the final analysis none of them can guarantee that the figures obtained reflect the time of sedimentation or early diagenesis of the sediments.

The isochronous dependences that we derived correspond to two stages of epigenetic transformations of the rocks: 1300-1500 million years. It is natural to suppose that formation of the sediments occurred earlier than 1500 million years, and, consequently, their stratigraphic position needs to be radically revised. Another important question concerns the scale of secondary chemical transformations of the rocks. One has to believe that there are or were natural processes that involve enormous volumes of rock in chemical transformations. The primarily carbonate composition of thick strata of preVendian deposits in Siberia makes these rocks extremely conservative in relation to their chemical and isotopic composition. This may be the reason for the homogeneous isotopic composition of oxygen and carbon in the investigated carbonates. Only in the isotopic composition of strontium is migration of material from terrigenous rocks to carbonate ones clearly recorded, which led to contamination of the carbonates with radiogenic strontium.

Large-scale secondary reworking of the rocks was manifested ~ 1.5 million years ago. It probably encompassed all of the strata of "Riphean" deposits. High original concentrations of strontium in the carbonates and the enormous thicknesses of the latter provided, to some degree, for preservation of parts of the cross section with isotopic ratios of strontium close to the original ratio. These ratios were very low (~ 0.704) and similar to those in rocks of the same stratigraphic level in the Kotuikan cross section. Such low isotopic ratios of strontium cannot be reconciled with the Riphean age accepted for these rocks. Unfortunately, it is not possible to determine their age exactly, and we can only indicate its probable limits: 1500-2000 million years. Judging from the initial isotopic ratios of strontium, their true age is closer to the lower limit (2 billion). On the Aldan shield, metasedimentary rocks of the Khani graben [12] and the Udokan series [1, 35, 36, unpublished data from the laboratory of isotopic geochemistry and geochronology of the Geological Institute of the Russian Academy of Sciences] possess such an age. Therefore, the question arises, are not so-called "Riphean" deposits of the Siberian craton a stratigraphic analog of Lower-Proterozoic deposits of the Aldan shield? If this is so, then the break at the foot of Vendian deposits that is noted everywhere in the Siberian craton may reach 1 billion years or more in time.

We realize that we are getting into a contradiction here with the results of stratigraphic research, which is hard to overcome. Resolving it will obviously require a great deal of work on both sides.

There is one more important question regarding the problem of correlation of Vendian—Lower-Cambrian deposits. The sharp peak of negative values of $\delta^{13}\text{C}$ known near the "Proterozoic-Paleozoic" boundary is also found in the cross section of the Katanga saddle. It can be called preManykai [23] and is a promising interregional stratigraphic reference. We believe that at that time there was an emission into the atmosphere of additional amounts of carbon dioxide — a product of oxidation of organic matter. This important problem, of course, needs further study.

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LOWER AND MIDDLE-JURASSIC DELTAIC SEDIMENTARY COMPLEX OF THE NORTHEAST CAUCASUS

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In the article, we discuss depositional environment of a thick deltaic sedimentary complex formed by a large paleoriver in the northeast part of an early and middle-Jurassic water basin in the Greater Caucasus. We show that a cyclical structure is typical of the deltaic sediments; large-scale cycles arose as a result of the influence exerted on the sedimentary process by periodic transgressions alternating with episodes of advancement of the delta into the basin. The conditions of formation of various textural features of the deposits are discussed.

The study of the structure and evolution of deltaic sedimentary complexes is important both for the discovery of general patterns of formation of such complexes and for clarification of the geological evolution of the specific areas where these complexes are located. In this regard, the thick (multi-kilometer) sequence of deltaic deposits in the Northeastern Caucasus is of appreciable interest, since it shows the long-term dynamics of a succession of sedimentary environments against the background of the evolution of a large sedimentary basin in the Greater Caucasus during the early Alpine stage of the basin's development.

Various aspects of the structure of the Lower and Middle-Jurassic, primarily coal-bearing, sequences of Dagestan have been discussed by many geologists [1, 4, 9, 11, 13, 16, 19, etc.], but the most detailed and thorough investigations of the Upper Toarcian-Aalenian deposits have been carried out by Frolov [17, 18], who reconstructed their depositional environments and demonstrated the important role of an ancient delta in the formation of certain sedimentary intervals.

Lithological-facial investigations of older Liassic deposits have only recently been conducted. To a significant degree, this has been a consequence of the lack of a reliable stratigraphic scheme. This part of the sequence was also formed under the influence of the delta of a paleoriver controlling sedimentation over the entire territory of Dagestan and adjacent areas. Lithological-facies investigations became possible after development of a detailed stratigraphic scheme for J_{1-2} in the Northeastern Caucasus [10, 14] carried out over a period of eighty years; this is the scheme used in the present report.

In addition to investigation of vertical sections, it was necessary to follow certain sedimentary units over almost the entire width of the territory in order to carry out lithological-facial reconstructions. In this connection, analysis of individual parts of a section could be carried out to different degrees of reliability: the Lower Toarcian deposits are exposed only in the deep gorge of the Avarsk Koysu River and, to a minor degree, in the Andiysk Koysu river gorge; on the other hand, Upper Toarcian and younger deposits can be traced over a substantial area.

The principal study area for the detailed lithological investigations included the Avarsk Koysu river basin, where the most complete section of J_{1-2} is located, and the Karakoysku river basin (Middle Toarcian-Aalenian); in other areas (the Samur, Rubas-Chay, and Kurakh-chay rivers, Sala-Tau ridge, the Andiysk Koysu River, etc.), we investigated sections of individual suites.

THE PALEOGEOGRAPHIC ENVIRONMENT IN THE NORTHEAST CAUCASUS AT THE END OF THE TOARCIAN-BEGINNING OF THE AALENIAN

It is advisable to preface the description of our investigations with a brief characterization of the delta during the period of its greatest advance into the sea at the end of the Late Toarcian-Early Aalenian (Fig. 1) [17]. The area of coal deposition within the territory of the delta was maximally developed at this time. According to the Frolov's estimates, the area of coal-bearing deposits is no less than 20,000 km² (only a third of it is exposed at present). This is comparable to the area occupied by the delta of the present-day Volga. Coal-bearing deposits accumulated in the environment of the land part

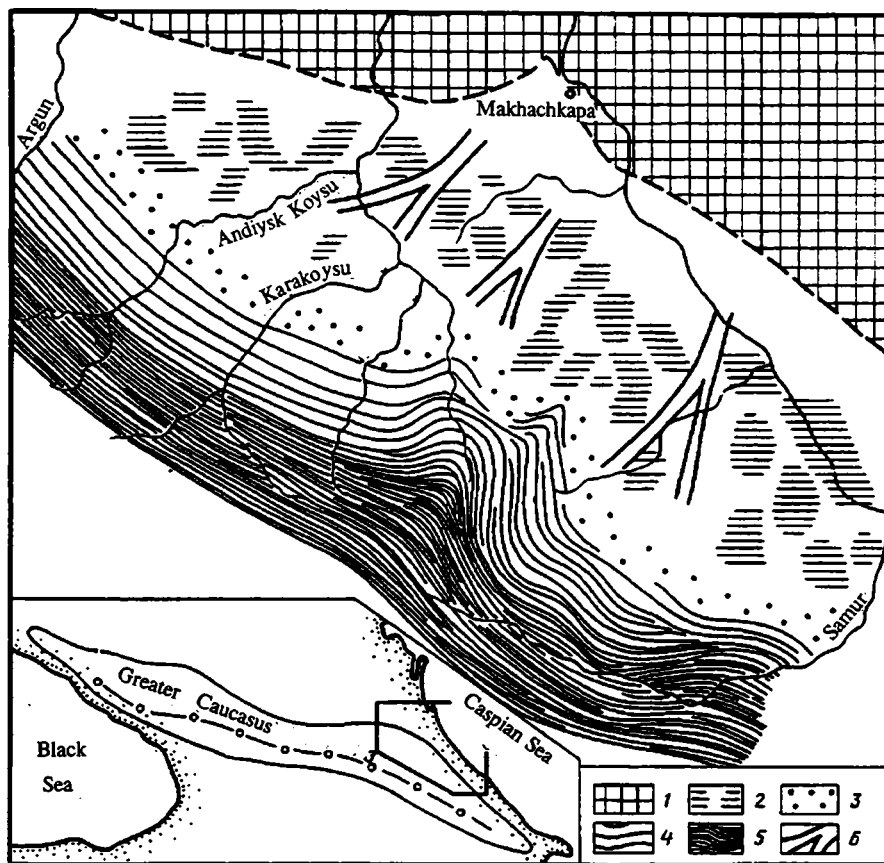


Fig. 1. Paleogeographic map of the Dagestan delta of Late Toarcian-Early Aalenian times (according to [17], with modifications by the author) and locations of deposits of the deltaic complex within the present-day structure of the Greater Caucasus: 1) dry land; 2) delta plain; 3) sand-bar belt; 4) submarine part of the delta (the avandelta); 5) deep-water part of the basin; 6) proposed positions of delta arms.

of the delta and coastal plain. The area of deltaic sedimentation seems to have divided in two by a large gulf (Khosreksk); this is indicated by a sharp bend of facial boundaries in the vicinity of the Kazikumukhsk Koysu river basin. It is important to note that, near the southwestern boundary of the coal-bearing beds, there are arenaceous deposits (up to 90-95% sand content) which extend in a relatively narrow strip from the southeast to the northwest through most of Dagestan (see Fig. 1). They composed a nearshore sand barrier. The position of the barrier on a facial profile, together with a combination of numerous lithological indicators, allow us to classify the conditions of its formation as an environment of strong nearshore currents, bars, offshore beaches, spits, shoals, shoreline beaches, and lower-course deltaic channels [17]. For the most part, sediments were deposited in an subaqueous environment under shallow-water conditions. To the southwest, these deposits grade into typical marine deposits.

Note that the sediments of the nearshore sand barrier were formed under the influence of powerful currents resulting from river discharge, on the one hand, and wave action and longshore currents, on the other. The interaction of these processes, each of which played an important role in supplying and reworking sedimentary material, was responsible for both the shape of the delta and the internal structure of the sequence formed. According to a classification of deltas [8, 20] based upon relationships between various hydrodynamic processes, the Dagestan delta can be classified as a delta in a region of interaction between fluvial and wave processes. Despite the fact that the character of the delta may have changed in many respects over time, its general features apparently remained the same over most of the Liassic.

Accumulation of sediments on the land part of the delta and its submarine part (the avandelta) proceeded against a background of rapid and uneven subsidence of the bottom of the basin as well as short-term eustatic fluctuations of sea level. The interrelationship of these factors influenced the location of the delta within the area, causing it to retreat or advance into the sea; this governed the character of sedimentation within the region.

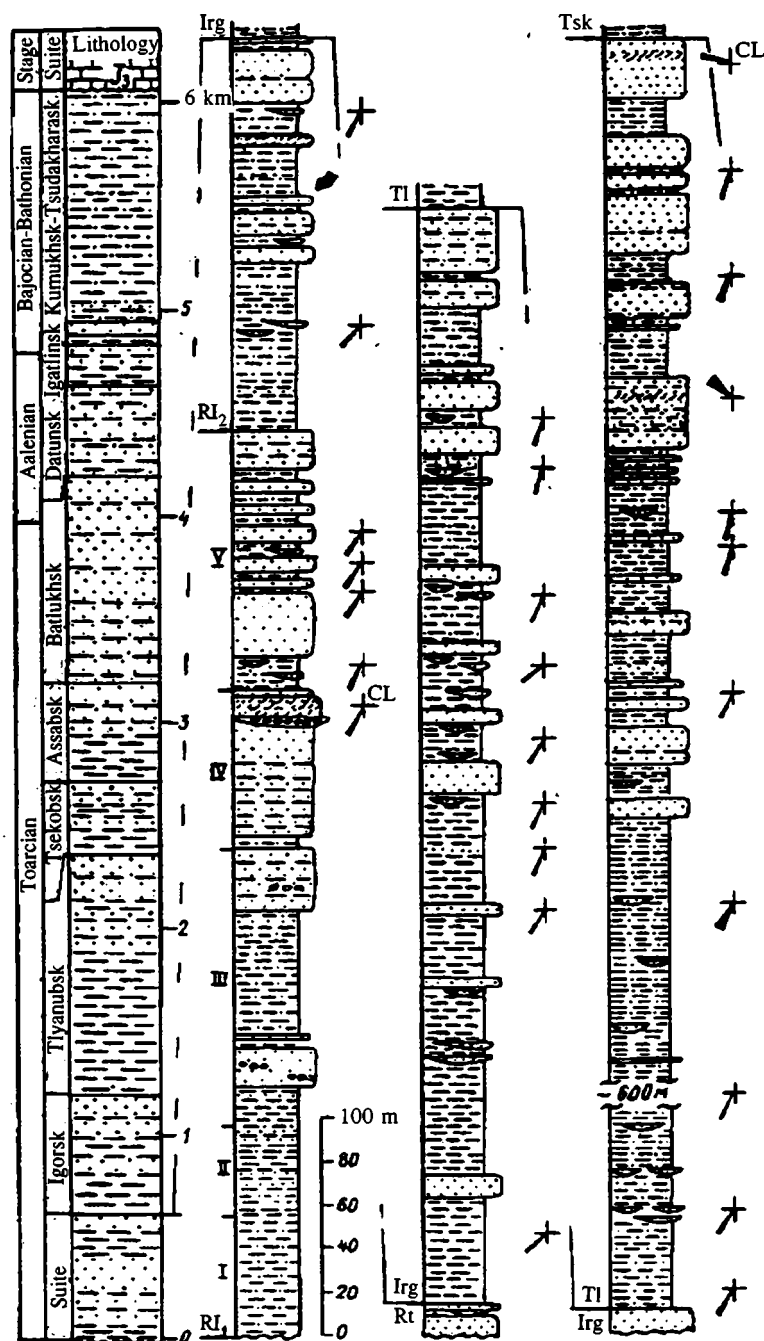


Fig. 2. Overall composition of the Upper Liassic-Middle Jurassic sequence of Central Dagestan (the Avarksoye Koysoy River) and the structure of the Toarcian-Aalenian suites: 1) conglomerate; 2) sandstone; 3) sandstone with unidirectional crossbedding; 4) predominantly aleurolitic rock; 5) predominantly clayey rock; 6) coal beds and carbonaceous siltstones; 7) trough-shaped sand bodies lying in clayey-silty deposits; 8) directions of paleocurrents measured according to the orientations of trough-shaped sand bodies; measurements obtained on the basis of direction of dip of cross-laminations in beds with unidirectional cross-lamination, indicated by the symbol CL. Suites: Rt) Ratlubsk; Igr) Igorsk; Tl) Tlyanubsk; Tsk) Tsekobsk; As) Assabsk; Bt) Batlukhsk; Dt) Datunsk; Igt) Igatlinsk; Km) Kumukhsk.

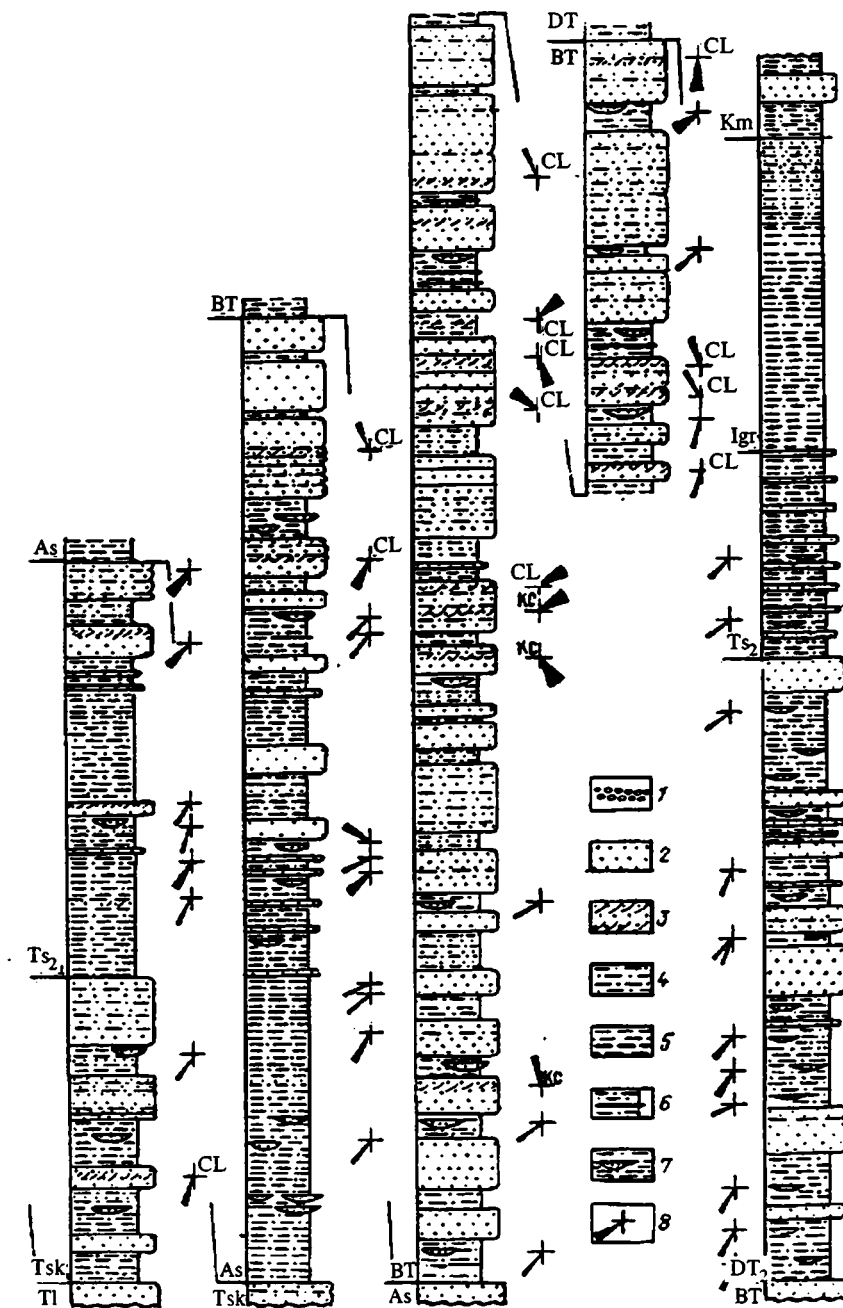


Fig. 2 (continued)

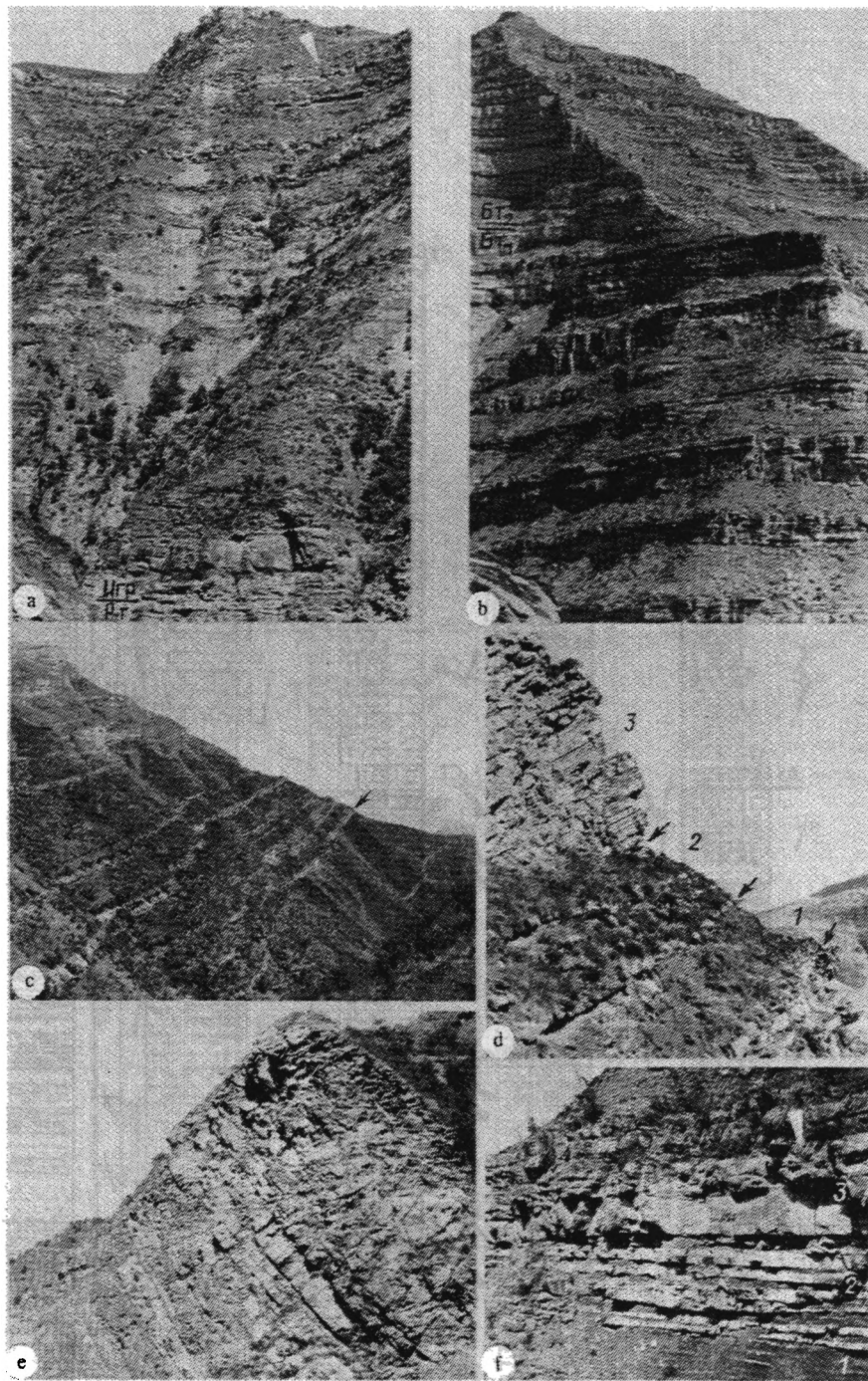


Fig. 3. Sedimentary cycles identified in the Lower- and Middle Jurassic of the Dagestan sequence: a-c) first-order cycles: a) structure of the Igorsk (lrg) suite, at the bottom, a sandstone bed in the roof of the Ratlubsk (Rt) suite; b) structure of the Batlukhsk (Bt); c) structure of the Tliyanubsk suite - top of the lower clay sequence, transitional part (boundary between them is marked with an arrow); 1-3) parts of a cycle (1: lower clayey part lying upon sandstone in the roof of the preceding cycle, 2: middle part, an interstratification of sandy and clayey-silty beds and lenses, 3: sandstone at the roof of the cycle, thickness of cycle ~20 m (boundaries between parts of cycle shown by arrows); e) cycle in the roof of the Ratlubsk suite (the Temir-Or River); f) cycle of the lower part of the Tsekobsk suite: 1) lower clayey part; 2) interstratification of beds of clayey and arenaceous rock; 3) sandstones in the upper part of the cycle; bed with unidirectional cross-lamination is marked by an arrow.

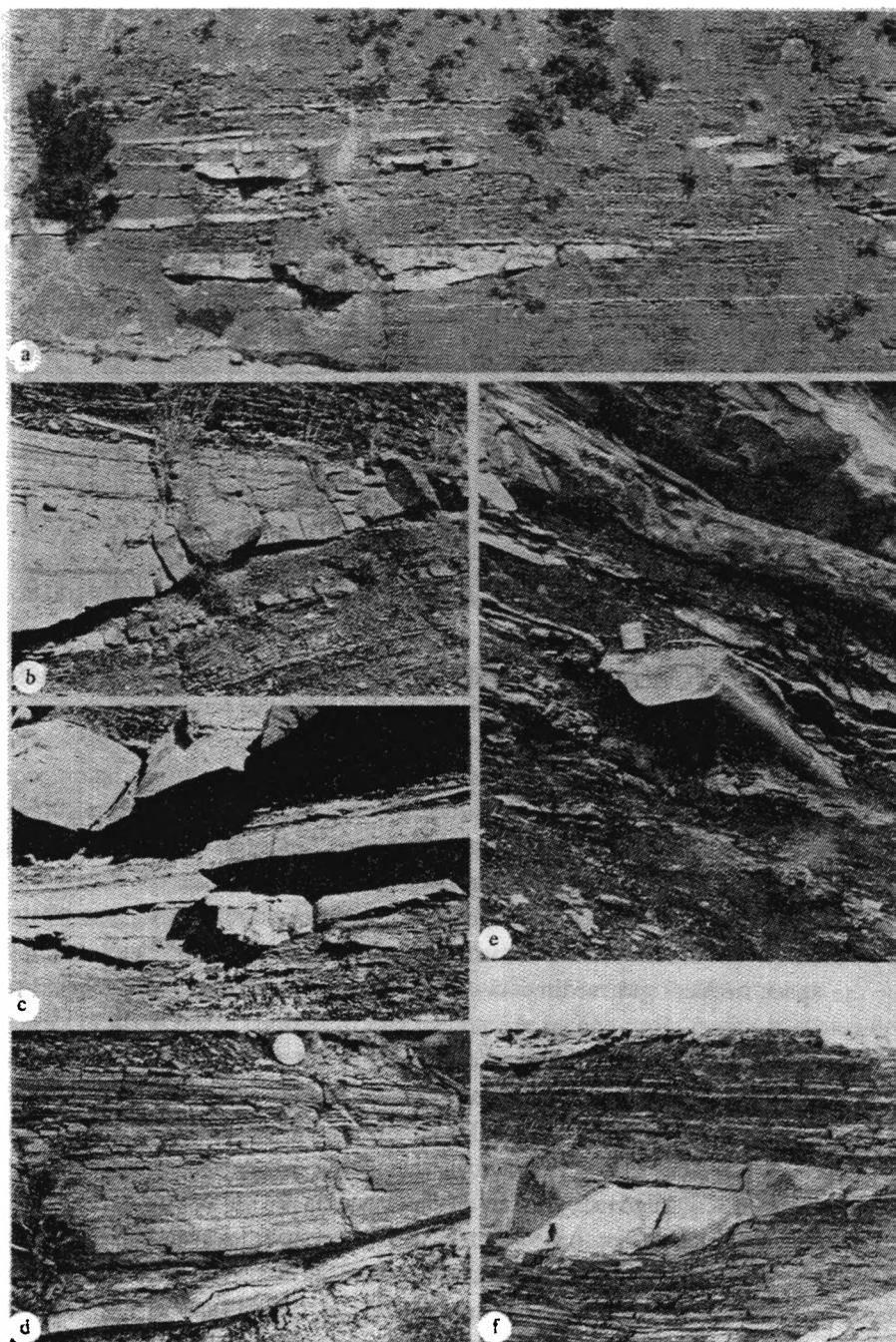


Fig. 4. Trough-shaped sand bodies from different parts of the Liassic-Aalenian sequence. a, b) Tlyanubsk suite (a: horizon with sand lenses, which, in the region closest to the unsubmerged part of the delta, correspond to a sandstone horizon; b) single lens, length of pick: 0.6 m); c) Tsekobsk suite, thickness of lens 0.45 m; d) Igorsk suite, lens consists of a series of separate layers (~ 30), diameter of the cover for the objective 4 cm; e, f) Datunsk suite (size of field notebook 10×15 cm).

GENERAL CHARACTERIZATION OF THE STRUCTURE OF THE TOARCIAN-AALENIAN SEQUENCE

Cyclical structure is typical of the Toarcian-Aalenian sequence (Fig. 2, 3); cycles of no less than three orders of magnitude can be distinguished. The largest cycles (first-order cycles) reach thicknesses of several hundred meters (see Fig. 3a-c) (exceeding 1 km in several cases) and can be traced over the width of the area. They serve as a logical start-

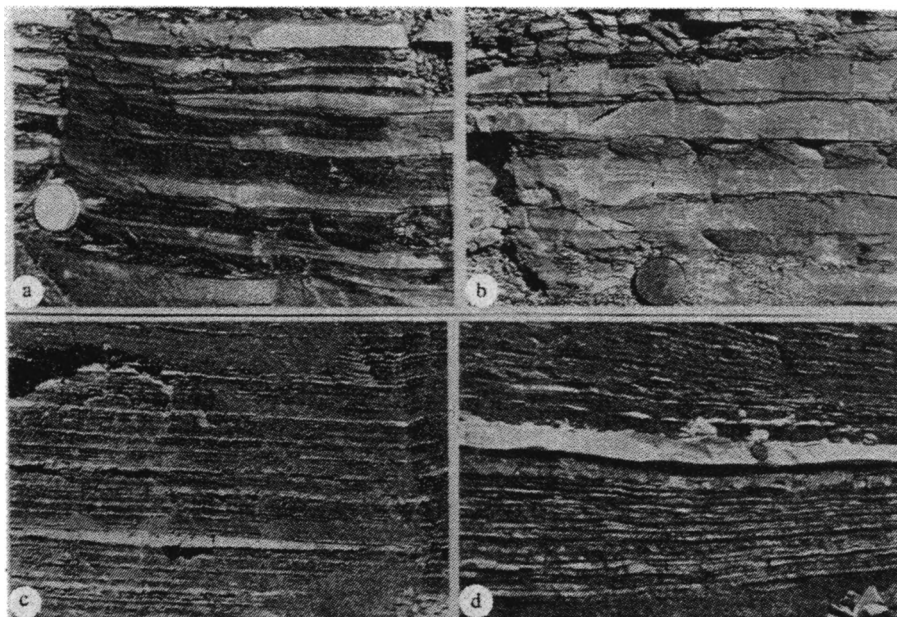


Fig. 5. Structure of clay-silt deposits from various parts of the Liassic-Aalenian sequence: a) Ratlubsk suite; b, c) Tsekobsk suite; d) Datunsk suite; clay-silt sediments deposited relatively close to the unsubmerged part of the delta.

ing point for division of the sequence into suites or subsuites. These cycles are similarly structured. Clayey deposits predominate in the lower parts; they contain relatively sparse and thin sandstone beds. Upward along the section, the number and thicknesses of sand bodies increase and the proportion of clayey deposits decreases; i.e., the upper parts of cycles are substantially more arenaceous. Thus, a more or less clearly expressed regressive type of structure is characteristic of the cycles. The formation of first-order cycles was associated with periodic rapid downwarping of the basin floor and compensatory filling of the space created with sediments of the delta, especially, the submarine part of the delta, the avandelta.

Within these cycles, one can usually distinguish second-order cycles fairly clearly; they vary in thickness from 10 m to several tens of meters. They are also characterized by a regressive type of structure (see Fig. 3d-f). Cycles begin with predominantly clayey or clayey-silty deposits, which are replaced upward along the section with packets showing interstratification of clayey-silty and sandy beds and lenses, occasionally taking on a flyschoid appearance. As a rule, sand bodies overlie deposits showing evidence of scouring; i.e., the feet of these bodies are quite typically erosional in character. Sand bodies of trough-shaped shape are frequently confined to intervals of interstratification (Fig. 4); their axes are oriented in a southwestern direction, i.e., approximately transverse to the strike of the basin's slope. Based upon the bedding of the sandstone beds and lenses, we can infer that sedimentation took place under conditions of fairly active hydrodynamics and that the beds were formed as a result of repeated pulses of incoming sandy material, usually accompanied by partial scouring of earlier deposited sediment. The cycles are topped by sandstone beds in which there are intervals where both massive varieties and sandstone spit into individual layers can be identified. The lamination in the beds is predominantly horizontal or gently oblique, but packets of layers with unidirectional cross-lamination are also present (see Fig. 3f). These sandstones also formed under conditions of active hydrodynamics [3, 15]. Proportions of the lower, middle, and upper parts of the cycle can vary substantially in certain cases; also, individual elements of a cycle are occasionally missing. In addition, their overall structure persists over the entire section of the Toarcian-Aalenian sequence. Formation of cycles of this type is a result of advancement of zones of sand deposition into the more marine parts of a basin, in particular, with progradation or lateral migration of sand lobes.

Finally, thin and frequently interstratified silt and clay layers ranging from fractions of a centimeter to several centimeters in thickness constitute the smallest sedimentary manifestation of the cyclicity (Fig. 5). Within these elementary cycles, one often finds a gradational structure, a relatively smooth transition from silty layers at the base of a cycle to

clayey layers further up; at the same time, silt layers lie upon clay layers of the preceding cycle with a sharp, occasionally clearly erosional break. The thickness ratio of clayey to silty layers in an interbed is variable. Cyclicity of this type is typical of most of the Toarcian-Aalenian sequence in the Northeast Caucasus. Very fine cyclites cannot be distinguished against its background. Within the region of the Dagestan delta (the more westerly areas of the Northern Caucasus), deposits of this type are either absent or compose relatively small intervals. Based upon the restriction of such cyclites to the area of the avandelta and the absence of very small-scale cyclicity, we believe its formation can be attributed to periodic annual and seasonal (flood-related) variations in the composition of suspensions supplied to the water basin by the Dagestan River, i.e., these deposits can be considered rhythmites [3, 12]. They are, as it were, background deposits against which layers accumulated as a result of supply of coarser terrigenous material from the land-based part of the delta by relatively vigorous currents (see Fig. 5c). In packets of flyschoid appearance, the rhythmites form "clay" layers alternating with interlayers of fine-grained sandstones. In relatively shallow-water areas of the avandelta, silty material frequently predominated, but, as a result of reworking by long-shore currents, the silt layers acquired a lenticular appearance (see Fig. 5d).

LITHOLOGICAL-FACIES CHARACTERIZATION OF THE DEPOSITS AND CONDITIONS OF THEIR FORMATION

The oldest member of the Toarcian section* is the Ratlubsk suite, which has been determined to be Lower Toarcian in age on the basis of rare ammonite finds; it corresponds to the *H. falcifer* zone [14]. The suite consists of two first-order cycles (corresponding to two subsuites); their thicknesses in the stratigraphic section are 380-400 and 190-200 m. The Lower Ratlubsk suite deserves special attention, since it is characterized by the most complete set of deposits formed in diverse depositional environments. Within the section of the subsuite, one can distinguish several parts (from the bottom upward) exhibiting substantial structural differences from one another (see Fig. 2).

I. At the base of the section, there is a sequence (apparent thickness ~60) consisting of an interstratification of clayey-silty and sandy layers. Gentle cross-lamination is characteristic of the sandstones. At the tops of beds, there are often ripple marks and inclusions of small pebbles of quartz and erosional products of local sedimentary rock, leaf imprints, and stems of land-dwelling plants. The thicknesses of sand bodies can vary along strike (from several centimeters to 0.5 m). Evidence of active bioturbation of the sediment is widely occurring in this stratum.

II. The sequence (35-40 m thick) consists of two incomplete second-order cycles in which upper sand bodies: at the bottoms of the cycles, argillite with thin (several millimeters) lenticules of silty material succeeds the underlying deposits along a sharp boundary; upward, they pass into an interstratification of argillite and siltstone (over several centimeters) and the cycle is topped by a packet of interstratified argillite and fine-grained sandstone (up to 0.3 m). These deposits, in turn, are overlain by a subsequent cycle of similar structure along a sharp boundary. The lamination in the sandstone is primarily horizontal; ripple marks and burrows of mud-eaters can be found occasionally at the roofs of beds.

III. Deposits of this interval form two complete second-order cycles: at the bases, there are packets of clayey-silty interlayers; in the middle portions, there are lenticular interlayers and sandstone bodies, frequently with erosional bases and, finally, the cycles are topped with thick (25-30 m) sandstone bodies which are fine- and intermediate-grained and typically well sorted; the lamination is gently oblique or horizontal. Both massive sandstones and sandstones split into beds (up to 1-1.5 m in thickness) and occasionally separated by interlayers of clayey-silty material can be identified. In the sandstones, there are frequently lenticular interlayers (up to 10-20 cm in thickness) of small-pebble conglomerate at various levels and also inclusions of pebbles in sandstones outside these lenses. Pebbles are primarily represented by quartz, quartzite, effusive rock, and, more rarely, crystalline schists. Similar sandstones are typical of the remaining part of the suite.

IV. At the topmost, predominantly sandstone part of the subsuite, a large-scale cycle with a structure different from the others holds a special place. It begins with a packet (11 m) of clayey-silty interbedding which, in the upper part, is replaced by an alternation of clayey-silty and sandy beds. A packet (~35 m) of predominantly sandy deposits contain-

*The contact of the Ratlubsk suite with older Upper Pliensbachian deposits is tectonic; reliable stratigraphic contacts are yet to be established.

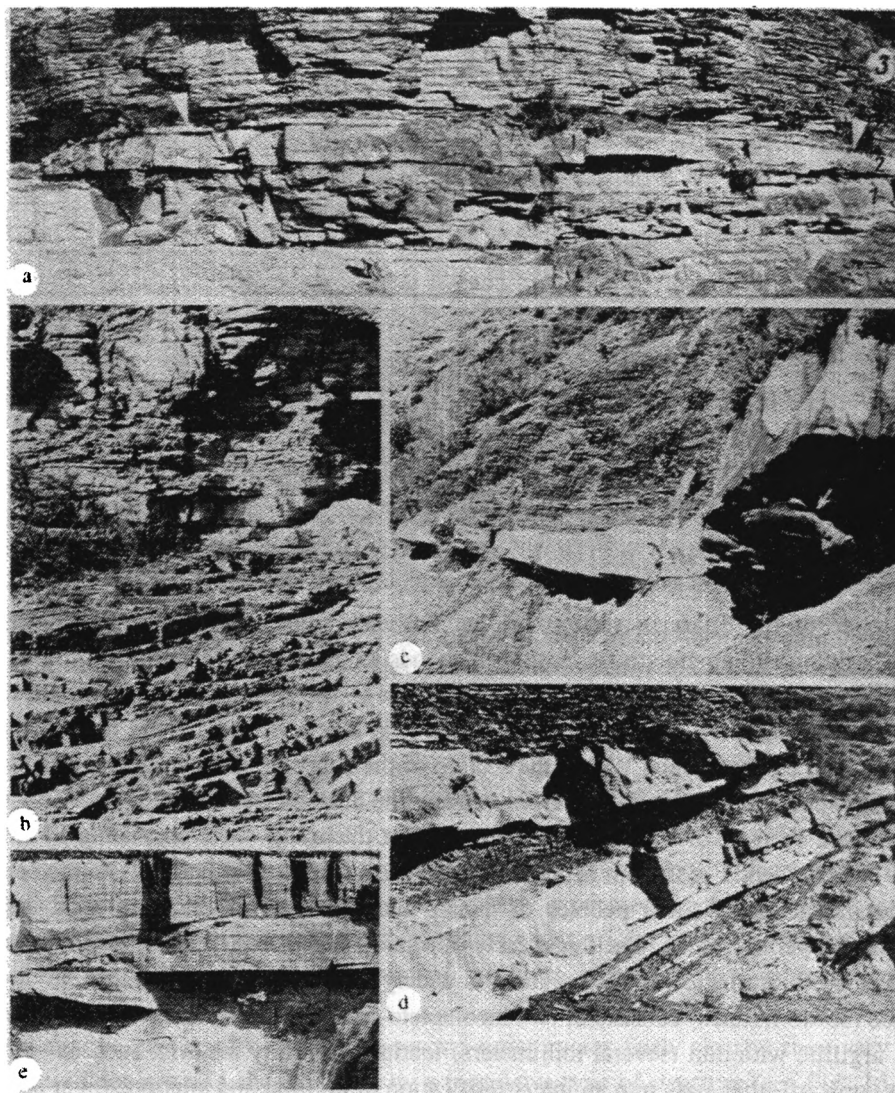


Fig. 6. Structure of parts of the avandelta series: a) gravellite-conglomerate lens, marked by arrows (2) and lying upon gently or horizontally laminated sandstone (1) and overlain by a packet of coarse-grained sandstone with multi-stage unidirectional cross-lamination (3); b) sandstone with multi-stage unidirectional cross-lamination; boundary with overlying packet of horizontally and gently cross-laminated sandstones marked by a bar; length of hammer (marked by arrow) 0.6 m; c) sandstone body bed with variable thickness along strike, formed by grain flow; at base) structures associated with intrusion into underlying clay sediments (noted by arrow); under the bed, deposits are homogenized, above the bed, distinct sedimentary layering is preserved; d) sandstone body formed as a result of several pulses supplying sandy material, with evidence of scouring of previously deposited sediments; e) sandstone bed formed by several pulses supplying sandy material and split along strike.

ing interbeds of clayey-silty rock at several levels lies above; it is overlain by well sorted sandstones without clayey interbeds (~ 15 m) (Fig. 6a, 1). In this sandstone, along a sharp erosional boundary, there is a large (up to 5 m thick) lens extending along strike for no less than 100 m (see Fig. 6a, 2); it is composed of gravellite, small-pebble conglomerate, and coarse-grained sandstone. Within the lens, one can distinguish several levels with unidirectional cross-lamination; lamina dip toward the southwest. Above this lens, there is a packet of fine-grained sandstone (10 m) characterized by multi-stage unidirectional cross-lamination (see Fig. 6a, 3; b); cross-lamina dip 230° SW; individual beds with unidirectional cross-lamination reach thicknesses of 1.2 m, but, in the upper part of the interval, they thin to a few decimeters. This cycle

terminates with a packet (~4 m) of horizontally laminated sandstone lying upon subadjacent deposits with a distinct erosional boundary. In turn, they are superceded by clayey-silty deposits of the base of the next cycle.

V. In the upper part of the Lower Ratlubsk subsuite (100-110 m), one can identify approximately seven cycles in which the thicknesses of sand bodies range from 5 to 30 m and generally decrease upward along the section. Splitting of the sand bodies into separate beds separated by clay interbeds increases in this direction. Horizontal lamination or gentle cross-lamination is type of the sandstones; they are fine- or intermediate-grained. The roof of the Lower Ratlubsk suite is a sharp contact; clayey-silty deposits of the base of the Upper Ratlubsk subsuite, with traces of intensive bioturbation of sediments, overlie sandstone of the upper horizon.

In terms of structure, the Upper Ratlubsk subsuite is generally similar to the lower part of the Lower Ratlubsk subsuite and correspond to packets I-III (Fig. 2).

In the more southerly sections of the Ratlubsk suite, i.e., in deposits which formed in the more marine areas of the basin, the structure of the suite persists and there is an increase in the thicknesses of clay interbeds separating sandstone horizons; the latter become less monolithic and frequently split into separate beds separated by clayey-silty interlayers. The numbers of lenticular layers of the conglomerates is the same in the sandstones; horizons with unidirectional cross-lamination are absent.

The structure of the suite, the material composition of the deposits, and their structural-textural features suggest their formation as a result of gradual seaward advance of the delta of an ancient Dagestan river. The lower horizons of the Lower Ratlubsk suite (Packet I) were deposited in the environment of a relatively shallow water basin, probably along its shelf portion (Packet II). The first indications of advancement of the delta were associated with the formation of reduced cycles without sandstone horizons in their upper reaches (Packet II). The occurrence of a first cycle with a thick sandstone horizon in the section suggests substantial seaward advancement of a sand lobe or even the entire delta front. After this strong pulse of sandy material supplied to the water basin, deposition of sandy sediments was abruptly reduced and, over time, formation of predominantly clayey-silty sediments with subordinate quantities of sandy sediments took place. The change in depositional environment may have been the result of a temporary retreat of the zone of deltaic sandy sedimentation or (if advancement of the delta took place in individual lobes) with displacement of the area of deposition of sandy material to adjacent areas due to lateral migration of a sand lobe. Subsequently, when the delta front advanced, the stage of predominantly sand deposition (packets IV and V) began. Sandy material supplied to the water basin was reworked by waves and longshore currents; this caused the deposits to be well sorted and also caused the type of lamination (horizontal or gently oblique), the presence of ripple marks, lenticular interlayers of conglomerates, etc.

The stage of maximum advance of the delta was the period of formation of the gravellite-pebble lens and packet of coarse-grained sandstones with multistage unidirectional cross-lamination (Packet IV). The lack of reliable signs of subaerial deposition allows us to attribute the formation of these deposits to submarine scouring extending into the area of the avandelta from one of the channels of the unsubmerged delta located relatively close (possibly within several kilometers) to the area where observations were carried out. Sediments deposited at that time are the coarsest-grained in the entire section of the Ratlubsk suite. Shifting of channels carrying coarse terrigenous material took place in a southwesterly direction (230° SW), as evidenced by the dip directions of cross-laminae. After the action of a channel ceased, the upper part of the deposits it formed were eroded by wave action and currents and the previous depositional regime was restored, as a result of which fine- and intermediate-grained gently cross-laminated sands along the erosional boundary overlie deposits with unidirectional cross-lamination. This sedimentation regime persisted for the most part until the end of early Ratlubskian times: sedimentary material in sand strata were reworked by marine longshore currents and wave action [3]; substantial accumulation of sediments due to a large-scale fluvial system from the shore side did not take place. The most probable cause of this type of deposition was retreat of the delta toward the northeast; however, we cannot exclude the possibility of lateral migration of the forward parts of the fluvial system into adjacent areas of the water basin.

Let us turn our attention to the following trend: whereas direct evidence of unidirectional currents from land are lacking in the more or less thick sand horizons, the existence of currents once directed toward the southwest can be inferred from the clayey-silty packets on the basis of the erosional bottoms of sandy lenticular interlayers and trough-shaped sand bodies (see Fig. 2). This is a result of the fact that stages of deposition of clayey and sandy packets differed substantially with respect to hydrodynamics of the environment: the pattern was one of relative calm during the formation of the lower parts of rhythms (clayey packets) and one of much more intensive forces (wave action, currents) during deposition of sand horizons, when repeated reworking of sedimentary material resulted in erasure of current marks on the landward side of the delta.

As the delta advanced, change in the hydrochemical composition of the water in the basin probably took place. Greater freshening was associated with the time of formation of sandstones with multistage unidirectional cross-lamination and the sediments found with such sandstones. These changes affected authigenic mineral formation: maximum sideritization of sediments coincided with sediments being deposited under conditions of relative freshening, whereas, the rocks of the lower and topmost parts of the Lower Ratlubsk sequence, there are fairly numerous small pyrite concretions.

The period of transition from the Lower- to Upper-Ratlubsk deposits was marked by an abrupt change in depositional environment: from predominantly sandy deposition to clayey-silty; this was accompanied by a decrease in the rate of sediment deposition and development of intensive bioturbation of sediments. This abrupt change may have occurred as a consequence of a brief but rapid transgression substantially affecting the position and activity of the delta, which probably shifted toward the northeast. Subsequently (as the transgression came to an end), renewed supply of large quantities of sandy material by the river resulted in growth of the delta and gradual advancement of the delta into the water basin. During late Ratlubskian time the trend of depositional changes generally repeated the trend for the first half of the early Ratlubskian: from predominantly clayey cycles with negligible enrichment with sandy material in their tops (an analog to Packet II) to cycles with thick sandy horizons (an analog to Packet III) (see Fig. 3e). However, sandstones with multi-stage cross-lamination are lacking here, although there are individual beds with unidirectional lamination. Thus, the Late Ratlubskian stage of deposition, like the preceding stage, was characterized by formation of sediments under conditions of delta advancement into more marine parts of the basin. During this time, however, the delta did not advance as far into the sea as during the preceding stage.

The structural similarity between the Lower and Upper Ratlubskian sequence suggests similar conditions of formation. But, whereas we can examine the Upper Ratlubsk subsuite in its entirety, the contact between the Lower Ratlubsk and the underlying stratum is missing. Never the less, in analogy with the Upper Ratlubsk subsuite, we can fairly confidently assume that deposition of the Lower Ratlubskian sediments began against a background of transgression, which subsequently ended and was replaced by the opposite process: advancement of the delta into the water basin and formation of the sandstone part of the section. As was discovered later, most of the suites in the Liassic-Aalenian section are structurally similar to the Lower- and Upper-Ratlubsk strata, so they probably also have a transgressive-regressive pattern of origin also.

The Igorsk suite, dated as the *H. bifrons* zone of the Lower Toarcian [14], reaches a thickness of 550 m in the stratotype section in the Avarsk Koysu river valley. In terms of structure and size, the suite corresponds to a first-order cycle (see Fig. 2, Fig. 3a). Clay deposits at the base of the suite lie on Upper Ratlubskian sandstones along a sharp boundary. The lower part of the suite (250 m) is more clayey than the upper part. A single sandstones horizon, a relatively thick one for this part of the section, extends 50 m from the base of the suite; others are no more than several meters thick. In the upper part of the suite, sand bodies are thicker, but the clayey intervals separating them are thinner; this is expressed in relief at the top of a 150-m sequence. Horizontal or gentle cross-lamination is typical of the sandstones; we did not find beds with unidirectional cross-lamination. Almost all the sandstone bodies were topped by rhythmically patterned intervals of layers typical of sections of prograding sand lobes (see Fig. 3d). Fine-grained deposits are represented by rhythmites — intercalations of clayey and silty layers, but the proportion of the clay component in the interlayers is larger here than in the Ratlubsk suite.

The formation of the Igorsk suite, like the suite discussed previously, began with a transgressive pulse, primarily due to downwarping of the basin floor. Despite the fact that a distinct shift of the delta, probably to the north-east, occurred as a result of transgression, its effect upon sedimentation continued to be pronounced: over the entire time of the suite's formation, advancement of sand lobes into the water took place periodically (no less than 10-12 times). However, active marine hydrodynamics caused reworking and redistribution of the sandy material supplied, as a result of which, beds with unidirectional cross-lamination were not preserved in the sand horizons. The trend toward increasing thicknesses of sand horizons and overall increasing sand content of deposits suggests that gradual seaward advancement of delta took place. However, whereas differences between clayey deposits at the bases of cycles in the Lower and Upper Ratlubskian subsuites and the sandstones in the upper parts of such cycles stand out in contrast, analogous cycles in the Igorsk suite show much less contrast in relief; this is probably a result of less substantial advancement of the delta during this time than during the preceding stage.

A comparison of synchronously formed horizons in different sections of the suite reveals changes in the suites in the direction from the shore to the more marine parts of the basin. Thus, some relatively thin (several meters) sand horizons are replaced by clay deposits containing lenticular or trough-shaped sand bodies just 3-4 km from the shore.

Similar changes can be found proceeding from the area near the source of sandy material and active reworking of such material by wave action and currents, which have formed continuous sand blankets, to the zone of predominantly clay-silt sedimentation, where currents bearing sandy material divided into separate streams excavating channels in clayey muds for their flow and carrying sedimentary material even farther down slope. The orientations of these common trough-shaped sand bodies in the section of the suite suggest a southwest direction of current (see Fig. 2 and Fig. 4d), i.e., the same direction found for the Ratlubsk suite. Intensive downwarping of the basin floor increased the southwest slope of the basin; this, together with high rates of sediment deposition [17] and periodic earthquakes accompanied by downwarping, caused instability in the positions of sedimentary masses at the surface of the delta fan. This resulted in downslope gravitational transport of large sand sheets, creating layers of stripping and homogenization of deposits beneath such beds [6]; the sheets themselves preserved their original sedimentary structure for the most part. In other cases, the same set of circumstances may have led to downslope stripping of unconsolidated sand masses; this may have created grain flows. This transport of sandy material and its reworking at lower levels of the slope resulted in the formation of beds of unstratified sandstone with variable thickness along strike and evidence of intrusion of sandy material into underlying clayey-silty sediments (see Fig. 6c). Sand accumulations of this nature formed almost instantaneously and lay on water-encroached unlithified clayey sediment; this, in turn, may have caused further instability of sedimentary masses at the surface of the delta fan. Occasionally, a sandy layer created in this manner was transported certain distance downslope, whereas sediments beneath the sandy layer were mixed and homogenized (see Fig. 6c). It should be noted that when sandstone beds (up to ~ 1.5 m) were created as a result of influx of sandy material via more or less constant and long-term currents which actively eroded the upper, the most water-encroached portion of sediment and sandy material lay upon already partially consolidated deposits, the position of a sand bed would have been subsequently more stable and transport of the bed downslope would not have taken place.

A comparison of the conditions of formation of the deposits of the Ratlubsk and Igorsk suites indicates that, in the sequence Lower Ratlubsk of Upper Ratlubsk subsuite of Igorsk suite, each subsequent stratum accumulated in an environment further from the land part of the delta.

The Tlyanubsk suite has been dated on the basis of ammonites as belonging to the top of the *H. bifrons* zone of the Lower Toarcian and the *H. variabilis* and *Gr. thouarsense* zones of the Upper Toarcian [14]. Deposits of the suite lie with a shape boundary on sandstone at the roof of the Igorsk suite. The thickness of the stratotype section on the left bank of the Avarksoye Koyusu River reaches 1150 m. In the J_{1-2} section, the deposits of the Tlyanubsk suite are the most clearly expressed first-order cycle (see Fig. 2, 3c). This is a cycle which can be broken down into two parts differing substantially in structure. The lower part (a thickness of ~ 750 m), is predominantly composed of clay rocks. The main (background) type of deposit, as in the older suites, is a rhythmic interlayering of silt and clay layers (usually 15 to 25 of such small rhythms per 1 m thickness of deposit). There are also four thin (less than 3 m) but relatively persistent sandstone horizons within this sequence. Sandy, trough-shaped bodies with erosional bases cutting into underlying deposits are most typical of the section of this sequence (see Fig. 4a, b); they maintain the previous spatial orientation in a southwestern direction. These trough-shaped bodies are usually confined to certain levels and form chains; within a layer, the distances between them can vary from several to tens of meters. In cases when several layers with lenses are located near one another (several meters or less), one can discern a fairly distinct trend: lenses at different layers are grouped in such a way that one stacks upon another (see Fig. 4a); occasionally, there is some westward displacement of overlying lenses. Sand bodies of this type are diverse in shape, ranging from flattened lenses several to tens of times longer than they are high to lenses which more or less isometric in cross-section and pipe-like in appearance; trough-shaped bodies with sharp and deep cuts into the underlying rock are frequently asymmetrical. For the most part, similarly shaped formations lie within a single layer. The depth of erosional cutting by sand troughs depends substantially upon the lithological composition of the underlying deposits, in particular, upon the presence of sandy and concretionary interlayers within them, interlayers which can prevent cavitation of rill channels. Stratification in trough-shaped sandstones is diverse, including horizontal or gently inclined layers accordant with the path of the trough bottom (see Fig. 4), cross (angled) abutment of layers with trough walls, etc.; repeated mutual cutting of one system of layers by another is frequently found. In almost all cases when the layered structure is preserved in sandstones of this type, we can infer infilling of erosion channels as a result of many repeated pulses supplying sandy material. In some thin (several decimeters) sandstone beds, the layering also suggests repeated cutting of lenses in a previously existing accumulation of sandy sediments, as a result of which, several beds constitute, as it were, a single system of conjugated sand lenses (see Fig. 6d).

Sparse sand horizons in the lower part of the Tlyanubsk suite, together with the clay packets, sand lenses, and interlayers underlying them form small (10-20 m) progradational cycles.

Large numbers of sandy horizons are characteristic of the upper part of the Tlyanubsk suite (~400 m) as opposed to the lower. In this part of the suite's section, however, two strata can be distinguished in turn. The lower, which can be considered transitional (approximately 200 m), is an alternation of clayey-silty packets and sandstone horizons 3-10 thick. The sandstones are horizontally laminated or gently cross-laminated, frequently contain interlayers with inclusions of locally eroded rock fragments (usually diagenetic siderite concretions washed from clay sediments). Numerous authigenic iron-carbonate concretions formed directly in sandstone are found in them also. The clay packets typical of the entire section consist of an interlayering of mudstone and siltstone layers. In contrast to the lower part of the suite, there are fewer trough-shaped sandstones here, but their orientations preserve the previous orientation: 210-230° SW.

The suite's section is topped by a stratum (200 m) consisting of four large sandstone horizons locally separated into several sandy packets by clayey-silty interlayers. Sandy horizons, together with clayey-silty packets, form large (40-80 m) progradational cycles. In many respects, these sandstones are similar to sandstones of the lower lying Igorsk suite, but are distinguished by the presence of beds with unidirectional cross-lamination; the dip directions of layers in different beds and horizons range from southwest to northwest. Accumulations of terrestrial plant fragments are frequently found on bedding planes in the sandstones.

Deposits of the Tlyanubsk suite can be traced over a substantial area. As a result, it is possible to assess the changes in the suite over area.

A comparison of sections along the Avarsk Koysu separated from one another by 5-6 km indicates that, while there is appreciable similarity in structure, there is also a substantial reduction in the thickness of the suite (from 1100 to 720 m) toward the north-east, with the thickness of the upper sandstone part reduced to a great degree. The variations in thickness we discovered lie almost precisely transverse to the strike of the paleobasin slope.

The section of the Tlyanubsk suite along the Karakoysu River, located 25 km southeast of the section along the Avarsk Koysu River, also shows substantial structural similarity; the difference consists only in some increase in the thickness of the suite along the Karakoysu an account of clayey-silty intervals between sandstones. In one of the sandy horizons here, there is a characteristic packet with multistage unidirectional cross-lamination, with lamina dipping toward the southwest (~220°). However, in individual beds with unidirectional cross-lamination in the same horizon, the dip directions of layers vary from south-southeast to west-northwest. In the section of the upper part of the suite along the Karakoysu River, there are many more trough-shaped sandstones than in analogous deposits along the Avarsk Koysu. The numerous siderite concretions are confined to clay packets here.

An analysis of the structure of the Tlyanubsk suite suggests that the trend of the sedimentary process was generally similar to that of the preceding cycle, but much greater contrast between different stages in the formation of the suite emerged during Tlyanubskian time. The beginning of the suite's formation was marked by a powerful transgressive pulse, as a result of which the Dagestan delta shifted to the north-east; this substantially altered the regime of delta activity for a long time. In the sedimentation, this was expressed in an abrupt change in types of deposits, from sandstones in the upper reaches of the Igorsk suite to predominantly clayey-silty deposits of the thick lower part of the Tlyanubsk suite. The slowing of sedimentation rates during the initial stage in deposition of the suite favored ichnofauna and bioturbation of sediments. Subsequently sedimentation rates increased and then remained more or less stable over the duration of the early Tlyanubskian. Periodic, pulsed, seasonal supply of clayey-silty material to the basin caused the formation of background small-rhythm deposits of interstratified silty and clayey layers. Assuming that the thicknesses of rhythms average 2-5 cm, the rate of deposition of such sediments can be estimated as 20-50 m/thousand years; when postsedimentational compaction is taken into account, these figures increase 1.5-2 fold.

The supply of sandy material to the basin during the early Tlyanubskian was limited, but some quantity was constantly arriving to the basin, as is indicated by the numerous sandy trough-shaped bodies. The surface of the fan of the Dagestan avandelta, as in analogous localities of present-day sedimentation [20], was covered by a multitude of small channels along which water carrying terrigenous material flowed. Sandy material was also supplied pulse-wise, as the infilling of sand troughs in the form of series of individual layers suggests (see Fig. 4). Distributing channels may have existed for a relatively long time, since trough-shaped sand bodies stacked approximately one on top the other formed lower along the slope. The occasionally noted westward displacement of upper troughs relative to those below was probably caused by erosion of the western sides of troughs and some extension of the troughs in this direction as a result

of the Coriolis effect. The formation of asymmetrical sand troughs which gradually deepened with shifting of the thalweg to the west during the stage of downcutting into the underlying deposits was apparently a result of the same effect.

After comparing the depositional environments of several morphologically similar trough-shaped sandstones located in the Ratlubsk suite and the lower part of the Tlyanubsk suite, we can conclude the following. In the first case, when sedimentation was governed by the influence of a delta advancing far into the water, erosion of previously deposited sediments and downcutting of channels into them took place by the action of vigorous currents which were continuations of the river flow itself and which were characterized by fluvial energetics. Therefore, erosion of clayey-silty deposits and infilling of troughs with sandy material took place almost simultaneously, as a result of one or several current pulses (the sandstone in the troughs is massive or divided into two-four layers). During the Tlyanubskian, formation of troughs and their infilling with sandy material took place far from the landward part of the delta, in a relatively deep part of the avandelta, where currents were not directly driven by the pressure of the river discharge; their energetics were mainly governed by gravitational force, i.e., they acquired an autokinetic character. In addition, it should be noted that troughs here are thinner than in the predelta zone. The generation of a profile of troughs and subsequent infilling of the troughs with sandy material were relatively long-term processes which took place as a result of multiple current pulses.

Over the duration of early Tlyanubskian time, there were episodes when the influx of sandy material increased, resulting in the creation of compact horizons with large numbers of trough-shaped bodies which represented the distal facies of sand lobes (see Fig. 4a). The latter only occasionally advanced into the basin and formed thin (a few meters) horizons which were fairly persistent along strike. In general, this time was characterized by relatively monotypic depositional environments.

During late Tlyanubskian time, the freshwater regime of sedimentation was altered and the rate of influx of sandy material to the basin began to increase; this was associated with the next advancement of the delta into the sea. Thus, the preceding transgressive stage was replaced by a regressive one. The upward variation in thicknesses and structure of sand horizons is evidence of this. During the first phase, relatively small horizons (3-10 m), corresponding to the frontal parts of sand lobes of the avandelta, formed. At this time, sedimentation processes were dominated by wave action and long-shore currents reworking and redepositing sandy material, as a result of which, horizontal lamination or gentle cross-lamination was created in sandstones. Subsequently, (during the phase of maximum delta advancement), four thick sand horizons were formed. The influence of river discharge was most strongly manifest at this time. In instances when its action created fairly powerful stream currents capable of vigorously eroding pre-existing accumulations of sediment and directed toward the deepened parts of the basin, packets of sandstones with multi-stage unidirectional cross-lamination in which lamina dipped toward the southwest were created (the Karakoysu river section); when currents were relatively weak, their directions were much more dependent upon the submarine accumulative relief, "wandering" of currents occurred, and monotypic beds with unidirectional cross-lamination and dip directions of layers ranging from south-southeast to west-northwest were formed. Also, the formation and preservation of sandstone beds with this type of layering (unidirectional cross-lamination) occurred more often in some instances and less often in others, but always episodically. In the zone of sedimentation, sandy material brought by current flows was subsequently reworked and redeposited by marine waves and currents and another type of layering was created in sandstones.

Formation of different parts of the suite took place against a background of varying basin depths. Maximum depths existed during the deposition of some parts of the clayey-silty sequence and, according to our estimates, may have reached several hundreds of meters. During the formation of the upper (predominantly sandstone) sequence, the basin depth was probably only several tens of meters and may have been less. However, we found no reliable indications of subaerial accumulation of sediments.

After comparing deposits of the upper part of the Tlyanubskian suite from different sections, we can attribute a number of their differing features to the presence of sandstones and multistage cross-lamination in the section along the Karakoysu River and the much greater number of trough-like bodies in clayey-silty deposits than are found in the section along the Avarsk Koyusu River. It seems to us that the most probably cause of this was the closer proximity of one of the large arms of the land part of the delta to the vicinity of the present-day Karakoysu valley.

In our opinion, the structural similarity exhibited by the Upper Tlyanubskian sequence over a large area and also the correlation between several structural features in synchronous sand horizons of different sections suggests common regional factors governing the development of the delta complex.

The Tsekobsk suite can be dated on the basis of ammonite finds as belonging to the upper part of the *Gr. thoursense* zone of the Upper Toarcian (see Fig. 2). The suite's section consists here of two relatively small first-order

cycles with thicknesses of 150 and 200 m. Despite the substantial arenosity of the lower cycle (almost half of its volume consists of sandstone), deposits of the Tsekobsk suite differ substantially in structure from the upper part of the Tlyanubskian suite, and the boundary between the two suites is well defined (see Fig. 2). In both the lower and the upper cycles, there are increases in the arenosity of the deposits from below upward and both cycles have a regressive appearance. A similar two-part structure of the suite can be traced in the section along the Karakoysu River. To the west (along the Andiysk Koysu River), the suite is primarily represented by thin-banded clayey-silty deposits with a packet (60-70 m) of laminated sandstone at the roof [14].

In the section along the Avarsk Koysu River, one can distinguish up to eight second-order rhythms ranging in thickness from 30 to 80 m; these rhythms are characterized by the presence of all the elements natural to progradational cycles: clay packets at the base of an interstratification of clayey and sandy beds (lenses) of sandstone horizons at the roof (see Fig. 3f). In the upper reaches of several horizons, there are beds of very coarse- and coarse-grained sandstone with unidirectional cross-lamination (with layers dipping toward the southwest), which lie, with a sharp erosional boundary, upon gently cross-laminated fine- and intermediate-grained sandstones. There are sandstone bodies which do not persist along strike but rather wedge out over several kilometers. Based upon the vertical profile of the rhythms and wedging out of sand bodies in a lateral direction, we can confidently assert that the formation of these cycles was associated with the progradational progress of sand lobes of the avandelta.

The thickness of the Tsekobsk suite is variable over the territory where it occurs and, as in the case of the other suites, increases in the direction of the more marine parts of the paleobasin. In the Avarsk Koysu river basin, the thickness of the suite increases from 350 to 500 m, i.e., by almost a third, over a distance of 8-9 km. These variations are primarily a result of increasing thicknesses of clay packets. In sections located several tens of kilometers to the west and corresponding to the more remote parts of the avandelta, the thickness of the suite increases to 700 m along the Andiysk Koysu and to 800 m along the Argun [14].

The structure of the Tsekobsk suite and its interrelation with underlying deposits suggests its formation as a result of two brief and relatively weak pulses, as a consequence of which the delta shifted a small distance to the north-east each time. At the end of the transgressive-regressive cycle, this was replaced by slight overall advancement of the delta into the basin. Because of its proximity, the delta continued to exert a very active influence on sedimentation in this region: advancement of sand lobes periodically occurred within the avandelta. These lobes repeatedly migrated laterally, in addition to frontal progradation.

Note that there are substantially more sandstone beds with unidirectional cross-lamination as well as tough-like sand bodies in the section of the Tsekobsk suite along the Avarsk Koysu River than in the section along the Karakoysu River. However, in the lower-lying Upper Tlyanubskian sequence, we find the opposite pattern: it is precisely in the section along the Karakoysu that we find sandstone packets with multi-stage cross-lamination and much larger sand troughs than along the Avarsk Koysu. This pattern is probably a result of the fact that one of the largest arms of the landward part of the delta, which influenced strong current flows, was located in the vicinity of the Karakoysu during late Tlyanubskian time, whereas, the suite had shifted to the west, to the vicinity of Avarsk Koysu by the time of the deposition of the Tsekobsk suite.

In the example of the Tsekobsk suite, the cyclicity of the sequence (two first-order cycles), which is well expressed in the proximal part of the avandelta (Avarsk Koysu), smooths out or entirely disappears in its distal parts (Andiysk Koysu, Argun). This is a result of the fact that advancement of the delta during the regressive phase of the cycle, for one reason or another, was fairly weak and did not lead to an increase in the arenosity of the deposits in the distal parts of the avandelta. Thus, the structure and degree to which cyclicity is expressed by the suite is, to a substantial extent, dependent upon position in the section relative to the landward part of the delta.

The Assabskaya suite belongs to the *D. levesquei* zone of the Upper Toarcian, as suggested by numerous finds of ammonites of *Dumorteria* ssp. [14]. Its deposits form a large first-order cycle (see Fig. 2) which is 500 m thick in the vicinity of the stratotype section along the Avarsk Koysu River. The lower and upper parts of the suite markedly differ in composition. The lower part (150-170) is replaced by sandstone along a sharp boundary at the roof of the Tsekobsk suite and is primarily represented by a small-rhythm (2-5 cm) interstratification of silty and clayey layers. The lower reaches of this stratum is characterized by the most numerous traces of sediment bioturbation (a similar pattern was discovered in other suites). The clayey-silty deposits are characterized by numerous siderite concretions; they form large concentrations in some packets, with layers of concretions occurring over 10-30 cm. Within the stratum, one frequently finds lenticular

interlayers and trough-shaped sand bodies compacted but without evidence of downcutting into underlying deposits. They show the southwestern orientation ($\sim 230-240^\circ$) typical of this section.

A transitional interval (~ 60 m) contains 12-15 beds (1-2 m) and lenses of horizontally laminated and cross-laminated sandstones, with some sequences of layers cutting the underlying beds. Along strike, some beds split into two or even more thin beds (see Fig. 6e). As a rule, the sandstone beds lie upon subadjacent deposits with some traces of scouring; within the sandstone beds, one finds siderite concretions washed from clayey sediments. The sole marks of the beds and the orientation of the sand troughs indicates the direction of the currents (west-southwest) associated with their formation ($245-260^\circ$), according to one measurement, $290-300^\circ$). Several packets of flyschoid appearance concentrate around the transition zone.

The upper half of the suite contains sandstone horizons which increase in thickness upward along the section; on the one hand, the clayey-silty deposits decrease from 25 to 3 m in the same direction. In addition to horizontally laminated and cross-laminated sandstones, there are beds with unidirectional cross-lamination here; the dip directions of layers vary from 220 to 320° .

The section of the suite located 7 km southwest of the stratotype section shows an increase in thickness from 500 to 720 m; its lower part shows a reduction in the number of trough-like sandstones.

Toward the east, in the Karakoysu river basin, the structure of the suite (~ 700 m) is generally the same as in the stratotype section, but substantial psammitization of the deposits is taking place. In the lower part of the suite, there sandstone beds appear (mainly up to 5 m in thickness); in the upper part, thicknesses of sandstone horizon can reach 60 m. These sandstone horizons contain both isolated beds with unidirectional cross-lamination and packets in which such beds form multistage series with layers dipping toward the southwest. Accumulations of terrestrial plant fragments can be found, however, there is no evidence of subaerial exposure. On the one hand, the composition of the suite south of the stratotype section (the Andiysk Koysu and Argun rivers) becomes more clayey, primarily as a result of partial wedging out of sand packets from the middle of the section [14]; the structure of the suite here is also generally maintained. In the Chanty Argun river basin in sections characterizing sediments deposited in parts of the basin more distant from the shore, the thickness of the stratum correlating with the Assabsk suite increases to 2500-2700 m on account of its lower part.

The structure of the Assabsk suite, like the structure of other similarly constructed strata in this region, suggests formation as a result of a transgressive-regressive cycle. A rapid transgression substantially altered the balance of sandy material brought from the land and clayey material in favor of the latter. In the clayey sediments, intensive rhythmic diagenetic layer formation proceeded, resulting in the creation of numerous interlayers of siderite concretions [5]. During the initial stages in the deposition of the suite, the depositional environment was relatively calm and favorable for the development of bottom fauna and bioturbation of muds. Subsequently, sandy material forming lenticular sand beds and trough-shaped bodies was brought into a region of predominantly clayey-silty deposition from the side of the land delta along a branching system of small channels (troughs). In this regard, the Lower Assabsk stratum is similar to the Lower Tlyanubskian.

Slowing or complete cessation of downwarping caused transgression to be replaced by gradual advancement of the delta, as a result of which the supply of sedimentary material to the basin increased and the upper part of the Assabsk suite formed.

The saturation of various sections with sandy material suggests that the delta arm supplying this area of sedimentation was located in the vicinity of the Karakoysu River, where the greatest arenosity of all parts of the Assabsk suite is found (to the west, in the direction of the Avarskoye River and farther along to the Andiysk Koysu River, the abundance of sandstone in the section gradually decreases). Further support for this conclusion includes the presence of sandstone packets with multi-stage unidirectional cross-lamination, deposited as a result of the action of relatively long-lived currents associated with a submarine continuation of river discharge and directed toward the southwest, toward the sea. Beds with unidirectional cross-lamination in the section along the Avarsk Koysu River do not form a multistage series and were linked to sporadically occurring, relatively short-lived and less powerful currents here, currents which may have changed direction from south- to northwest and which substantially depended upon external factors. Thus, having evaluated the hypothetical home-base of this part of the avandelta of an arm of the Dagestan River, we can see that, during the Assabskian, this part of the avandelta returned to approximately the same position which it occupied during the Tlyanubskian, from where it soon (the Tsekobskian) shifted to the west, into the vicinity of the Avarskoye Koysu.

The upper part of the Assabsk suite and the above-lying, thick avandeltaic and deltaic complex were formerly grouped within the Karakhsk suite; a detailed description of this and results of lithological-facial analysis are presented in

[17]. We will therefore only describe this stratum in general terms, using an updated and more detailed stratigraphic classification [14].

The Assabsk suite is overlain with a sharp boundary by deposits of the Batlukhsk suite, dated as belonging to the upper zone of *D. levesquei* of the Upper Toarcian and the *L. opalinum* zone of the Lower Aalenian on the basis of numerous ammonite finds [14]. The stratigraphic section of the suite in the Avarsk Koysu river valley (see Fig. 2) reaches a thickness of 1000-1150 m. The suite is fairly clearly divisible into two parts. The lower (510-630 m) part is an alternation of clayey-silty packets and sandstone horizons which, as a rule, combine to form a second-order cycle 25-35 thick. Typically, 1/2 or 2/3 of the thickness belongs to sandstone horizons (see Fig. 3b). In the upper part of the subsuite, the clayey-silty packets are thinner and the cycles become progressively less distinct. On the basis of underlying erosional cuts of sandstone beds and lenses occurring in clayey-silty deposits, we can infer a southwest direction (230-255°) of currents which carried sandy material; in one of the sandstone packets with multistage unidirectional cross-lamination, the layers dip toward the northwest (330-350°). In the upper sand horizon of the lower subsuite, several beds show cross-lamination with laminae dipping toward the northeast (50-70°). In sandstone horizons, fairly frequently one finds beds with unidirectional cross-lamination, with the numbers of such beds increasing upward along the section of the subsuite.

Thick (up to 30-40 m) massive sandstones which are separated by thin (a few meters, occasionally up to 10 m) clayey-silty packets are typical of the upper part of the Batlukhsk suite (500-530 m). The sandstones include numerous interlayers with pebbles of both quartzic and local rocks (fragments of siltstone, concretions washed from clay deposits). Beds with unidirectional cross-lamination are frequently found in the sandstones. Layers vary in their direction of dip from south-southeast to northwest (one occasionally finds such variation among different beds in the same sand horizon); layers dipping toward the northeast can also be found. In addition, troughlike sand bodies in clayey-silty packets, as before, indicate a current direction to the southwest (200-245°). In deposits in this part of the suite, one finds numerous accumulations of plant remains. There are also several beds (a few decimeters in thickness) of allocthonous coal and carbonaceous siltstone, as well as large (up to 2 m in length) sideritized fragments of tree trunks.

The upper part of the Batlukhsk suite is the thickest sandstone sequence in the entire J₁₋₂ section of the Northeastern Caucasus. The granulometric composition of the sandstones in the suite are also distinguished by their relatively high contents of very coarse-grained and coarse-grained varieties.

Toward the west, the thickness of the suite increases because of an increase in its lower subsuite (from 510 to 1000-1100 m in the Argun river basin); there is a concomitant increase in its clay content. In the upper subsuite, which maintains its thickness, there is also an increase in clayey-silty deposits and simultaneous disappearance of coarse-grained rocks and interlayers of coal [14, 17]. In general, these areas of the Batlukhsk suite maintain the appearance of a large-scale regressive cycle.

Southeast of the stratotype section, the structure of the suite shows some changes: in the upper reaches of the Kazikumukhsk Koysu, it consists of two large-scale cycles of regressive appearance; farther to the south-east (the interfluvium of the Samura and Chirakhchaya), the thickness of clayey-silty packets increases substantially; these packets separate sandstone horizons. The total thickness of the suite increases to 3500 m.

In this stratum, Frolov [17] identified deposits of a sand barrier dividing the deposits into longshore-current deposits, seaward fluvial drift, etc. In the area of greatest deposition of carbonaceous strata (southeast of the zone of the sand barrier), one can distinguish deposits of influent lagoon-type bays which shoaled current, occasionally lagoonal deposits, floodplain deposits, etc. In general, the depositional environment was fairly diverse.

A cyclicity of deposits not found in the other part of the J₁₋₂ section are characteristic of the Batlukhsk suite. Thus, in the area of carbonaceous strata, there are cycles [17] in the lower parts of which one finds coarse-grained, typically massive sandstone with coarse cross-lamination at the base and, in the upper parts of which, one finds wavy or horizontally laminated sandstone; upwards, they are replaced by flaggy sandstone, siltstone, and, finally, clayey rocks, commonly including coal beds which are predominantly allocthonous. These, in turn, are overlain by flaggy sandstone, typically ending a cycle. In addition, there are symmetrical, relatively clayey packets with coal cycles as well as "inverted" cycles with the reverse sequence of deposits. These cycles reach thicknesses of 30 m.

The overall trend of formation of the Batlukhsk suite was generally similar to that of the preceding suites: the abrupt transition from the thick sandstone stratum of the upper reaches of the Assabsk suite to a sequence of alternating clayey-silty packets and sand horizons of the Lower Batlukhsk subsuite suggest a successive transgressional pulse. The thickness of the suite is not less than 1000 m, therefore, its deposition must have been associated with rapid downwarping of the floor of the sedimentation basin. At this stage in the deposition of the suite, the downwarping caused some deviation

of the delta's advance toward the northeast; however, in comparison to the Tlyanubskian or Assabsk episodes, this transgressive pulse did not finally result in radical changes in the sedimentation regime and substantial shifts of the delta toward the northeast did not occur during that time. On the one hand, at the end of the first half of the Batlukhskian, rapid advancement of the delta into the basin began, reaching a maximum during late Batlukhskian time. This advancement of the delta took place at the approximate transition between the Toarcian and the Aalenian and was the largest-scale advancement for the entire lifetime of the deltaic sedimentary complex.

The Datunsk suite, lying upon the previous suite with a sharp boundary, has been dated on the basis of a *L. murichsonae* zone as Upper Aalenian [14]. In the vicinity of the Avarsk Koysu and Karakoysu, it is fairly clearly divisible into two parts (subsuites). The lower sequence is represented by ten second-order cycles in which thicknesses of sandstone horizons vary from 5 to 35 m and thicknesses of clayey-silty packets vary from 10 to 30 m (see Fig. 2). The presence of numerous eroded lenses, trough-shaped bodies (see Fig. 4e, f), and sandstone beds with sharp and deep scour rills on their bottoms, rills that cut into underlying deposits are frequently characteristic of the lower (clayey) units of the cycles. In general, they maintain a southwest orientation. In clay packets, there are frequent interlayers of siderite concretions; they are especially numerous at the bases of packets. Sandstone horizons, as a rule, consist of several packets of massive or flaggy sandstones, occasionally separated by thin (several decimeters — a few meters) clayey-silty deposits and siltstone fragments. Whereas sandstones with gentle cross-lamination (rarely unidirectional) predominate in the section along the Avarsk Koysu, there are both individual beds with unidirectional cross-lamination and packets with multi-stage unidirectional cross-lamination in several horizons in the lower part of the sequence in the section along the Karakoysu River (the thickness of such a packet in one of the horizons reaches 15 m). In all cases, layers dip toward the southwest. Fragments or accumulations of land-dwelling vegetation are frequently found in the deposits of the suite. The lower part of the suite is topped by a sandstone horizon (15 m, the Avarsk Koysu River).

The upper part of the suite (100-110 m, the Avarsk Koysu River) is distinguished from the lower by the lack of thick sandstone horizons: sandstone packets consist of series of beds (several decimeters) separated by clayey-silty interlayers. The beds frequently do not persist along strike, but rather wedge out. Sandstones lie on subadjacent deposits with a clear erosional boundary. Numerous trough-shaped bodies in clay packets are oriented toward the southwest (240-260°). The sequence is topped by a sandstone horizon (~5 m).

Toward the west (the Andiysk Koysu, Argun), deposits of the suite become much more clayey; sandstone packets persist only in the upper parts of the suite [14]. The lithological composition of the upper part of the suite begins to resemble that of the overlying clayey Igatlinsk suite. South-east of the stratotype section (the upper reaches of the Kazikumuksk Koysu, Chirakhchay, and Samur), the thickness of the Datunsk suite increases to 1400-1900 m, primarily on account of clayey-silty deposits. The Lower Datunsk suite (1000-1500 m) is represented here by an alternation of packets of clayey-silty rock, occasionally with sandstone beds (100-170 m) and packets of massive (15-40 m) sandstones [14]. In the clay packets, there are substantial accumulations of siderite concretions as well as interlayers of limestone-coquina containing remains of pelecypods, belemnites, and, occasionally, ammonites. The Upper Datunsk sequence (300-550 m) is represented by clayey-silty deposits with numerous lenticular sandstone beds and trough-shaped sand bodies, which are unevenly distributed along the section, along with several horizons (a few meters) of massive sandstone. Whereas the proportion of clayey-silty deposits increases toward the west and south-east, the quantity of sandy material substantially increases toward the north and north-east (sections of the suite within cores of the Izvestnyakoviy Dagestan anticline along the Ulluchay, Gamriozen', and Rubaschay rivers): sandstone horizons (15-35 m) alternate with packets of clayey-silty rock containing coal beds in places. Concurrently, the thickness of the suite decreases in these regions and is not divided into subsuites.

The abrupt transition from massive sandstones of the Batlukhsk suite to a sequence of alternating sandstones and clay packets of Datunsk suite can be traced over a substantial area and is due to the successive pulse of a transgression at this time. Taking into account that the Datunsk suite is clearly divisible into two parts, one is entirely justified in inferring the existence of two transgressive pulses. The first of these resulted in a substantial shift of the delta toward the north-east. This event affected sedimentation differently in different parts of the region. Thus, in the western (most distal parts), supplies of sandy material were sharply reduced and, accordingly, differences between the Upper Batlukhsk and Lower Datunsk sequences are most pronounced. At the same time, the region of sections along the Avarsk Koysu and Karakoysu rivers is much closer to the land delta, in connection with which deposits of the Lower Datunsk subsuite formed in a marine environment, but under strong influence of fluvial current (there are numerous indications of current erosion of previously accumulated sediments, including trough-shaped bodies, lenticular beds, concretionary conglomerates in sandstones, etc.). Packets with multi-stage unidirectional cross-lamination within the composition of sand horizons suggest

that currents directed toward the southwest (submarine continuations of river discharge) existed for a fairly long time in places within the zone of the proximate avandelta. The greatest number of such formations is found in the vicinity of Karakoyusu river section, near which one of the largest delta arms was apparently situated. The disappearance of a sandstone packet with multi-stage cross-lamination from the upper part of the section of the Lower Datunsk subsuite and the decrease in the thickness of the sand horizons here may indicate a gradual sideward movement of the delta and, accordingly, development of transgression over the duration of the entire Early Datunsk time, although at the end of this stage, the rate of the delta's advancement possibly slowed somewhat. The sandy material brought to the water basin was vigorously reworked by wave action and longshore currents; this caused the horizontal lamination or gentle cross-lamination in the sandstones.

The second transgressive pulse caused a substantial acceleration in the retreat of the delta; this resulted in a ubiquitous reduction in the supply of sandy material to the water basin (especially in the western part of the avandelta); however, the fairly vigorous current-related hydrodynamic activity regime in the central part of the avandelta persisted and thick sand horizons gave way to thin (several meters) packets which frequently split into several beds (several decimeters), occasionally of lenticular form. As in the preceding stage, monotypic conditions of sedimentation generally persisted over the course of Late Datunsk time, but at reduced levels. Next, disappearance of sand lenses cutting into the underlying deposits from the upper clayey packets suggests a gradual weakening of current hydrodynamics; this was apparently a reflection of a continued, but slowed transgression.

Thus, both of the Datunsk transgressive pulses differed from the preceding ones (such as the Tlyanubsk or Assabsk) in the fact that they finally slowed down, but did not weaken to the point that transgression gave way to advancement of the delta into the water basin and formation of more arenaceous deposits at the upper than in the lower parts of the sequences. In the beginning, these transgressive pulses were fairly rapid and accompanied by substantial alteration of the sedimentation regime relative to that during the preceding stage, but subsequently, the pulses slowed somewhat, though they continued to occur.

The Igatlinsk suite is assigned to zones of *L. muchisonae* and *Gr. concavum* of the Upper Aalenian and the lower reaches of the *S. sowerbyi* of the Lower Bajocian [14]. In the section along the Avarsk Koysu River (a thickness of 130 m), the suite can be clearly subdivided into two parts (see Fig. 2); the lower part is primarily represented by dark siltstones without distinct layering which lie conformably and with a sharp boundary upon the last sandstone horizon of the Datunsk suite, which shows abundant evidence of sediment bioturbation at its roof. Siltstones contain numerous interlayers of siderite concretions, several interlayers (a few decimeters) of concretionary conglomerates, and a limestone bed with fossil belemnites, pelecypods, etc. The upper part of the suite is represented by a sequence with a flyschoid appearance. It is an interstratification of beds (a few decimeters) of grey siltstone and fine-grained sandstone. Numerous burrows of crawling and burrowing organisms can be traced here. Toward the south-east, in the middle part of the suite in the section along the Karakoyusu River (190 m), there are two sandstone horizons (3-4 m) which, together with the underlying packets (5-7 m) of interstratified beds of siltstone and fine-grained sandstone form two small (10-12 m) characteristic cycles typical of sections in the leading parts of prograding lobes of the avandelta. Farther to the south-east, according to data presented in [14], the thickness of the suite continues to increase to 500 m at the headwaters of the Ulluchay River and along the Chirakhchayu River and to 950 m at the upper reaches of the Chirakhchay River and along the Samur River. Here, clay rocks play a determining role in the composition of the deposits and the overall structure of the suite persists. Besides interbeds, there are cycles characteristic of sections of prograding avandelta lobes in the upper part of the suite. North-east 40 km from the section along the Avarsk Koysu River, in the core of the Irganaysk anticline of Izvestnyakoviy Dagestan, there is an increase in arenosity of deposits as a result of the presence of sandstone interlayers in the lower part of the section. Here, there is also a single progradational cycle with a thickness of up to 25 m (the upper sandstone horizon is 10-m thick). It is interesting to note that, in contrast to the preceding suites, the thicknesses of these deposits are almost identical, despite the substantial distance between these sections. In the most westerly sections (in the Argun river basin), the lithological composition of the suite becomes homogeneous and consists of clayey-silty rocks.

The abrupt transition from the sandy-clayey deposits of the Datunsk suite to the siltstone of the Igatlinsk suite can be traced over a wide area and was caused by the successive transgressive pulse. Whereas the Datunsk transgression caused only a partial flooding of the extensive aggradation plain created during the previous stage, as a result of delta advancement into the water basin, The Igatlinsk transgression apparently covered the remaining area with sea and shifted the delta laterally toward the north-east for a substantial distance. Within the western and central parts of the region, a sea with monotypic depositional environments was created. In contrast to the preceding stages, this sea was characterized by

more or less calm hydrodynamic conditions. The vigorous southwest-directed currents directed associated with river discharge and so typical of earlier times were absent. As a result of predominantly fine clayey-silty material was deposited over an extensive area. Only during the second half of the Iगतlinskian, when the transgression had ended and the position of the delta had stabilized, did periodic influx of fine sandy material into the water basin begin; as a result of this influx, a flyschoid-like packet was created. The lack of textures associated with vigorous current flow on the bottoms of interbeds indicates that such currents played a minor role in the supply of sandy-silty material to this part of the basin. The calm environment in the water basin promoted the dispersal of bottom fauna; traces of their live activity can be found in the deposits of the suite. The stage of formation of the suite ended with a regressive episode accompanied by the formation of a horizon (a few meters thick) of calcareous, structureless, intensively bioturbated sandstone.

Toward the northeast (moving toward the delta), the supply of sandy material and the arenosity of deposits gradually increased. In the southeastern part of this area, in contrast to the western and central parts, the basin floor downwarped appreciably, as indicated by the increase in the thickness of deposits of the suite here. Probably, this part of the basin was geomorphically characterized by a decrease in the elevation of the basin floor. Not surprisingly, it is in this direction that currents carrying sandy material from the delta episodically penetrated and leading parts of thin sand lobes of the avandelta occasionally advanced. During Iगतlinskian time, as a result of transgression and shifting of the delta a substantial distance toward the northeast (or north?), the influence of the delta on sedimentation in this region decreased substantially overall and continued in a much weaker form than during the preceding periods.

During the Bajocian, a substantial geological restructuring of the entire Greater-Caucasus region took place. As a result of a powerful Early Bajocian transgression, the delta shifted hundreds of kilometers toward the north [7], influx of sandy material began, and a sedimentation regime came to dominate an extensive territory of Eastern Ciscaucasia.

* * *

Thus, it follows from the material presented above that the entire thick Toarcian-Aalenian clastic complex of the North-East Caucasus formed under the influence of a large river and consisted of an avandelta over an extensive territory. Vigorous currents caused, to a substantial degree, by river discharge, carried large quantities of sandy material in a predominantly south-westward direction from a land delta. Evidence for this includes trough-shaped sand bodies found almost along the entire section and oriented toward the southwest, beds with unidirectional cross-lamination, occasionally forming multistage systems with layers predominantly dipping in the same direction, etc. Sandy material brought by these currents was subsequently reworked and redistributed by wave action and longshore currents. Periodic advance and lateral migration of sand lobe of the avandelta or overall frontal advance of the zone of sand deposition were very characteristic of the deposition of the sequence. All of stratigraphic subdivisions of the Lower Jurassic, the Aalenian sequence, show very regular variations in thickness over the area: to the southwest, west, and southeast, their thicknesses increase, primarily as a consequence of increases in the thicknesses of clayey-silty deposits separating sand horizons. The latter, as is quite evident from a comparison of sections at various distances from the land part of the delta, split up toward the southwest (i.e., toward the sea); the numbers and thicknesses of clayey-silty beds increase within their structure. The absence of any thick sandstone beds within the Upper Toarcian deposits infilling the Bezhitinsk depression in the headwater region of the Avarsk Koysu River suggests that sand horizons wedge out toward the southwest. On the one hand, a clear trend toward increased arenosity is evident toward the northeast (in cases when one can trace coeval deposits in several sections); in the end, this resulted in a homogeneous sand composition of deposits and, accordingly, disappearance of cyclicity.

With respect to size and time of existence, the Dagestan deltaic complex has no analogs in other areas of the Caucasus basin, although undoubtedly smaller rivers flowed in from the surrounding territory and brought large quantities of sandy material to the sea, i.e., the depositional environment of this sedimentary complex differed markedly from that of other fans. Accordingly, the activity of the Dagestan River must have been different from that of the other rivers. Therefore, one could hardly attribute the existence of the Dagestan fan to the "activity" of even several relatively small rivers [17, 19]. The most plausible explanation is formation of the Dagestan delta as a consequence of the activity of a large river draining the East Caucasus and carrying substantial quantities of fairly mature terrigenous material. On the coastal plain, the river apparently divided into two large branches and a number of smaller ones. This resulted in the formation of two parts of a delta protruding into the sea but separated by a bay (to some extent, the morphology of the Dagestan delta was similar to that of the present-day Rhone river delta [20]). The fact that regional stratigraphic subdivisions can be traced

over a substantial area of the avandelta suggests formation of the delta over the entire area according to a single pattern associated with the activity of a single, main source of sandy material. Finally, besides the main river, smaller rivers flowing from the surrounding uplands may have participated in the formation of the delta. Some variations in the composition of the heavy fraction found in the south-east and north-east parts of the delta may be attributable to such smaller rivers [18, 19]. A similar pattern was discovered in the deposits of the productive sequence of an ancient delta in the territory of the Central Caucasus [2]: the paleo-Samur and other rivers draining the East Caucasus substantially affected the composition of terrigenous sediments in the western part of the paleo-Volga delta.

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DETERMINATION OF THE AGE OF HYDROTHERMAL FLUIDS BY THE KINETIC-GEOCHEMICAL METHOD

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An estimate of the age of hydrothermal fluids of rift zones of oceans and continents, island arc regions, as well as regions of mud volcanism and occurrences of condensation and solution waters of hydrocarbon accumulations is given on the basis of the chemical, gas, and isotopic compositions and geothermobaric conditions. Correlations between the degree of accumulation of trace elements in hydrothermal fluids and their age were established.

The occurrences of present-day hydrothermal fluids on the earth have been recorded at many points of rift zones of oceans and continents, in island arc regions, and in regions of mud volcanism. A study of their age is necessary for creating models of the development of hydrothermal systems, calculations of conductive and convective heat effects, alteration of rocks, for estimating the total quantity of chemical components carried to the surface, and processes of hydrothermal mineralization [8, 10].

The kinetic-geochemical method was developed by the authors in 1983 [21] on the basis of investigating autochthonous brines of the East Ciscaucasian artesian basin, and then was tested on material of the lower stages of other artesian basins of the former USSR [22].

The cation coefficient θ is used as the quantitative criteria:

$$\theta = (e \text{ Na}^+ + e \text{ Mg}^{2+})/e \text{ Ca}^{2+}. \quad (1)$$

The formula in the present interpretation was corrected with the use of the data of J. Peter et al. [33], who on the basis of the ^{14}C isotope determined the age of calcite and CO_2 of hydrothermal zones of the of the southern depression of Guaymas Basin, and is represented in the form

$$T_\theta = A_\theta \frac{\varepsilon_r}{\varepsilon_B} \lg \frac{\theta_0}{\theta} 10^{\frac{100}{\tau}} \pm 0.2T_\theta, \quad (2)$$

where T_θ is the age of hydrothermal fluids, tens of thousands of years; A_θ is a correction factor, the value of which increases with increase of the fluid temperature (T , °K) in the following way: 350 – 0.13; 370 – 0.19; 390 – 0.25; 410 – 0.32, and further according to the equation $A_\theta = 0.32 + (T - 410)0.004$; ε_r and ε_B are the exponential geochronotherm (EGCT) and chronobaric gradient (ECBG) – complex parameters taking into account the geothermal and pressure conditions of the hydrothermal object, the age of the rocks of which is taken in time units (T) equivalent to 10^4 years ($\varepsilon_e = 10^{\tau/1000}$; $\tau = t(^{\circ}\text{C})\log T$; $\varepsilon_B = 10^{B/1000}$; $B = 10P/\log T$). The initial cation coefficient θ_0 can be characterized by two values: 22 for hydrothermal systems of thalassogenic feeding (the maximum value for waters and brines of Neogene horizons [22]) and 42 for those of meteoric feeding (the fresh thermal water from well 38 in the region of Te Puke (New Zealand) having isotopic composition $\delta^{18}\text{O} = -5.5\text{‰}$ and $\delta\text{D} = -31\text{‰}$ is taken as the standard [36]).

By analogy with [21, 22] the root-mean-square error of the value of the age is 20%, it increases to 40% in the case of a predictive estimate of the undisclosed depths of the hydrothermal system.

Table 1 gives data for calculating the age of hydrothermal fluids in volcanic regions of rift zones. The hydrothermal fluids of mid-oceanic ridges are characterized in the basins Juan de Fuca, Guaymas, 21°N EPR, 13°N EPR, Galapagos rift zone, TAG 26°N, Manus, and Franklin. The age of the oceanic crust varies from $50 \cdot 10^4$ to $600 \cdot 10^4$ years, the ocean depth from 2200 to 4200 m, the temperature at the outlet of the hydrothermal fluids is from 275 to 350°C, the pressure of the column of ocean water is from 23 to 43 MPa, the values of EGCT from 3.40 to 9.38 and of ECBG from 1.24 to 1.68, mineralization of the thermal waters from 34 to 64 g/liter, cation coefficient from 3.4 to 15.4, correction factor from 0.87 to 1.17. The age of the hydrothermal fluids varies from $8 \cdot 10^3$ to $90 \cdot 10^3$ years. It should be noted here

TABLE 1. Characteristics of World Hydrothermal Fluids [2, 3, 5, 10, 13-19, 24, 25, 28-35, 37, 38]

Area of geothermal system (location)	Region	Age of rocks of hydrothermal object $\times 10^4$	Depth of occurrence, m	Temperature, °K	Pressure, MPa	EGCT ϵ_1	ECBG ϵ_B	Mineralization of hydrothermal fluids, M, g/liter	Cation coefficient Θ	Correction factor A_Θ	Age of hydrothermal fluids T_Θ
Regions of volcanism of rift zones											
Pluim	Juan de Fuca	600	2500 *	623	26,0	9,38	1,24	64,0	4,3	1,17	90 $\pm$ 18
		600	~5000†	~723	~50,0	17,78	1,51	140,0	5,0	1,57	163 $\pm$ 65
Mud Volcano	Yellowstone Park	100	spring	513	0,1	3,02	1,00	0,49	3,3	0,73	38 $\pm$ 8
Salton Sea	California rift	200	2100	633	17,0	6,73	1,19	258,0	1,57	1,21	113 $\pm$ 23
Sonoma		50	geyser	513	0,1	2,56	1,00	1,3	3,34	0,73	32 $\pm$ 6
Cerro Prieto		50	1700	593	12,0	3,50	1,18	19,8	18,2	1,05	16 $\pm$ 3
Gyayman		50	2500 *	588	30,0	3,40	1,50	38,0	3,5	1,03	28 $\pm$ 6
21° N EPR	East Pacific Rise	100	3900 *	623	40,0	5,01	1,58	34,0	15,4	1,17	8 $\pm$ 2
13° N EPR		100	2800 *	623	30,0	5,01	1,41	44,0	5,3	1,17	37 $\pm$ 7
Galapagos rift zone		100	4200 *	623	43,0	5,01	1,64	36,0	6,1	1,17	29 $\pm$ 6
TAG 26°N	Mid-Atlantic	50	3700 *	593	38,0	3,50	1,68	39,0	11,5	1,05	9 $\pm$ 2
Reykjavik	Iceland	150	1754	565	13,0	4,32	1,16	32,4	5,49	0,94	32 $\pm$ 6
Krable-Naumafjöll		60	2000	623	14,0	4,19	1,17	0,8	10,2	1,13	37 $\pm$ 7
Atlantis II	Red Sea rift	120	~4000	~543	~44,0	3,64	1,63	303,6	15,9	0,85	4 $\pm$ 2
Danakil depression	East African Rift	1000	~4000	~473	~52,0	3,98	1,49	300,0	13,8	0,57	5 $\pm$ 2
Allalobeda		1000	geyser	492	0,1	4,54	1,00	2,2	19,0	0,65	16 $\pm$ 3
Tanganyika	East African rift	1000	~1200	~573	~10,0	7,94	1,08	2,3	11,0	0,97	58 $\pm$ 23
Arshan	Baikal rift	300	~7000	~523	~70,0	4,16	1,92	4,1	0,64	0,77	46 $\pm$ 19
Bhuttayagudem	Godavari (India)	200	500	373	4,0	1,70	1,04	1,7	1,42	0,20	9 $\pm$ 2
Manus	Papua-New Guinea	400	2500 *	548	26,0	5,20	1,26	38,0	3,4	0,87	44 $\pm$ 9
Franklin		300	2200 *	583	23,0	5,86	1,24	53,0	12,4	1,01	18 $\pm$ 4

Regions of volcanic belts											
South Meager Creek	British Columbia	200	2500	503	25,0	3,38	1,28	3,1	13,1	0,69	14 ± 3
Ahuachapan	El Salvador	50	thermal field	501	0,1	2,44	1,00	15,1	12,5	0,68	6 ± 1
Calabozos	Chilean Andes	80	500	523	3,0	2,99	1,06	2,0	2,63	0,77	41 ± 16
Larderello	North Italy	370	3000	673	27,0	10,64	1,27	1,83	0,92	1,37	269 ± 54
Zephyria	Greece	100	1100	573	10,0	3,98	1,14	32,0	5,53	0,97	30 ± 6
Mutnovsk	Kamchatka	2200	1500	553	9,0	8,63	1,06	0,9	3,15	0,89	124 ± 25
Lower Kozheleva		1200	~3000	~643	~28,0	13,77	1,23	5,6—47	2,4	1,25	193 ± 77
Pauzhetka		1000	1200	483	7,0	4,27	1,05	3,5	14,8	0,61	18 ± 4
Paratunka		2200	spring	361	0,1	1,97	1,00	1,5	1,65	0,17	9 ± 2
Nachikinskoe		2000	370	357	3,7	1,89	1,03	1,2	9,3	0,15	3 ± 1
Nalychevskoe		2200	spring	348	0,1	1,78	1,00	3,8	4,0	0,12	4 ± 1
Uzon		100	*	366	0,1	1,54	1,00	1,05	4,9	0,18	5 ± 1
Ébeko Volcano	Kuril Ridge	50	*	367	0,1	1,44	1,00	19,8	1,41	0,18	6 ± 1
Mendelev Volcano		50	*	357	0,1	1,39	1,00	4,6	5,64	0,15	4 ± 1
Golovnin Volcano		50	*	371	0,1	1,47	1,00	2,4	1,46	0,19	8 ± 2
Arima	Japan	500	168	406	1,6	2,29	1,02	72,5	3,9	0,30	12 ± 2
Onikobe		900	1200	573	10,0	7,69	1,10	18,7	4,86	0,97	67 ± 13
Tamagawa		900	spring	371	0,1	1,95	1,00	4,8	1,51	0,20	10 ± 2
Wakura		900	*	368	0,1	1,91	1,00	20,4	1,09	0,18	8 ± 2
Matsukawa		900	1500	553	11,0	6,71	1,09	4,3	10,7	0,89	49 ± 10
Matsao	Taiwan	100	1500	563	11,0	3,80	1,14	23,8	3,4	0,93	37 ± 7
Manikaran	Himalaya	100	spring	370	0,1	1,56	1,00	0,56	2,73	0,19	7 ± 1,5
Chi Solok	Indonesia	100	*	368	0,1	1,55	1,00	1,1	4,6	0,18	5 ± 1
White	New Zealand	30	crater lake	373	0,1	1,41	1,00	97,3	7,32	0,20	3 ± 0,5
Wairakei		60	500	513	3,0	2,67	1,05	3,3	34,3	0,73	3 ± 0,5
Taupo		200	~5000	~823	~70	18,45	2,01	4,3	27,0	1,97	46 ± 18

*Ocean depth.

†Ocean depth + thickness of oceanic crust.

that the time of formation of the hydrothermal vent in the Guaymas Basin obtained by us $(28 \pm 6) \cdot 10^3$ years corresponds to the average ^{14}C age estimates of calcite inclusions – $20 \cdot 10^3$ years [33]. Various mechanisms have been proposed for explaining the salinity variations of fluids of the ocean floor geothermal systems. Experiments on the reaction of diabase and intruded seawater were conducted by J. L. Bischoff and R. J. Rosenbauer (1989) for reproducing earlier published observations of chloride depletion of the presumably forming short-lived chlorine-containing mineral. The absence of any chloride depletion according to the data of these investigations gives grounds to assume that the formation of chlorine-containing minerals is not widespread enough to explain the observed salinity variations of the oceanic hydrothermal fluids. Therefore, the given authors proposed some model of subcrustal circulation [28]. Instead of a simple single-flow convection system, consisting of two vertically nested convection cells in which brine is heated at depth and moves toward the overlapping chamber with ocean water. Such stratification of salinities is known as a process in the mechanism of fluids under the name double-diffusive convection. This process is provided by a stable high-temperature heat flow upward through the fracture front adjacent to the magma and by limited chemical exchange of brine with the overlapping ocean water, which explains the salinity variation and high content of metals in the fluid vents. Brine is formed as a result of two-phase separation of ocean water during magmatogenic-tectonic manifestations, accumulates and remains comparatively stable in the section directly under the magma chamber. The given process is examined with reference to the Pluum area of the Juan de Fuca Ridge, mineralization of brine in the lower cells here is predicted up to 140-200 g/liter, and the cation coefficient is about 5.0 (see Table 1). Consequently, at a depth of 5 km with a temperature $\sim 450^\circ\text{C}$ and pressure ~ 50 MPa the age of brine of the lower cells can be $(163 \pm 65) \cdot 10^3$ years.

An important distinctive feature of the gas composition of fluids in mobile zones of the oceanic crust is the high concentration of helium enriched in the light "primary" isotope ^3He in them. The value of the ratio of isotopes ^3He and ^4He , the so-called helium isotope tracer, is used for evaluating the presence of a deep-seated juvenile component in thermal fluids. Values of $^3\text{He}/^4\text{He}$ in units per 10^{-5} are characteristic for the present-day mantle. According to the data of B. G. Polyak, P. N. Tolstikhin, and V. P. Yakutsen, the helium isotopic composition in basalts and thermal fluids of rift zones of the World Ocean varies in a narrow range $(1.02-1.32) \cdot 10^{-5}$: Juan de Fuca Ridge, Guaymas Basin, 21°N EPR, 20°S EPR, Galapagos Rift (1°N), Mariana Trough, Mid-Atlantic Ridge (23°N). Along with the hydrothermal fluids of the Guaymas Basin, within the California rift fluids of the Salton Sea, Sonoma, and Cerro Prieto areas are characterized in an age respect. The slightly brackish thermal waters of the Sonoma geyser are clearly of meteoric feeding and have an age $(32 \pm 6) \cdot 10^3$ years, i.e., close to the time of formation of the hydrothermal vent of the Guaymas Basin.

V. I. Kononov [10] validly explains the origin of the Cerro Prieto hydrothermal fluids by the dissolution and leaching of evaporites by infiltration waters and effect of magmatic fluid. The latter is confirmed by the characteristic values of $^3\text{He}/^4\text{He}$ ($1.0 \cdot 10^{-5}$) and CO_2 content to 92.4%. This powerful hydrothermal system occurred $16,000 \pm 3000$ years ago.

Far older are the strong brines of Salton Sea ($T_\theta = 113,000 \pm 23,000$ years), which formed as a result of feeding mainly by salt waters of Salton Sea sinking along a fault and together with magmatic fluid ($^3\text{He}/^4\text{He} = 1.0 \cdot 10^{-5}$ and $\text{CO}_2 = 90.0\%$) dissolving the halogenic rocks of the section [10].

The approximately coeval (32,000-37,000 years) hydrothermal fluids of Iceland (Reykjavik and Krable-Naumafjöll) are distinguished by a higher proportion of magmatic fluid, since the ratio of helium isotopes is $(1.35-1.75) \cdot 10^{-5}$, the concentration of CO_2 is 55.3-93.6% and H_2 up to 44.5%.

According to the data of G. Yu. Butuzova [3], in the transition zone of the Red Sea rift, where the Atlantis II Basin is located, the hydrothermal process began 20,000-25,000 years ago. At early stages the process occurred rather sluggishly, which was reflected in the accumulation of biogenic and terrigenous deposits with an insignificant concentration of ore substances occurring directly on young (12,000 years) oceanic basalts. Hydrothermal activity in the basin began starting from that time, but some decrease of activity was noted later (~ 8500 -6000 years). Only in the Holocene has this section of the rift been in a highly active stage of development. According to our data, the age of the strong Atlantis II brines, the source of which is presumed at a depth of 4 km, reaches 4000 years, i.e., characterizes the most powerful manifestation of the hydrothermal process.

With the East African Rift strong brines of the Danakil depression also are the youngest (5000 years). The slightly brackish thermal waters of the Allalobeda geyser have an age of $16,000 \pm 3000$ years, and those of the Cape Banza lacustrine springs (northern part of the Tanganyika trough) with a depth of the roots of the hydrothermal system of ~ 1.2 km, even $(58 \pm 23) \cdot 10^3$ years.

V. V. Golubev, Yu. A. Zorin, S. V. Lysak, and S. V. Osokina established in the Baikal rift zone by analytical and numerical modeling that the observed distribution of the heat flow is explained by a fracture intrusion 5-10 km wide that rose to depths of 2-12 km along the axis of the rift 2-3 millions years ago. In the Tunka depression, where the top of the crystalline basement lies at a depth of 7 km with a temperature of $\sim 250^{\circ}\text{C}$, in the Arshan area in borehole 28 the helium isotope tracer is equal to $1.0 \cdot 10^{-5}$ and the CO_2 content is 94% [20]. The substantial effect of the mantle fluid makes it possible to predict the age of this hydrothermal systems as up to $(46 \pm 9) \cdot 10^3$ years.

In the Godavari rift valley (India) the slightly brackish thermal water from a well in the Bhuttayagudem area has an age of 9000 years. Its close relation to precipitation is confirmed by the predominance of nitrogen in the gas composition (71.5%), the deep-seated fluid is manifested by a concentration of carbon dioxide (24.9%), hydrogen sulfide (0.5%), and traces of hydrogen [35].

Hydrothermal fluids of volcanic belts of continental regions have been studied in areas of British Columbia, El Salvador, Chilean Andes, Northern Italy, Greece, and Himalayas (see Table 1).

The Meager volcanic complex includes a series of Pliocene-Quaternary andesite and rhyodacite eruptive centers which pierce the Jurassic-Cretaceous coastal plutonic complex of southwestern British Columbia (Canada) [29]. Slightly brackish water having an age of 14,000 years is found in a borehole in the South Meager Creek area at a depth of 2500 m with a temperature of about 230°C . The fluid of the Ahuachapan thermal field that occurred 5000-7000 years ago is distinguished by markedly elevated concentrations of CO_2 (50-80%) and hydrogen (10-40%). The Calabozos Caldera represents an extensive manifestation of silicate volcanism during the Late Pleistocene [30]. The mouth temperatures reach $80-98^{\circ}\text{C}$, and the water migrates from a depth of about 500 m, where the temperature is presumed equal to 250°C . The basis of the hydrothermal fluids of age $(41 \pm 16) \cdot 10^3$ years is meteoric water with isotopic composition $\delta\text{D} = -98$ to -89‰ and $\delta^{18}\text{O} = -13.5$ to -9.8‰ . In the Larderello region an intrusion with a temperature of $\sim 750^{\circ}\text{C}$ is presumed at a depth of 8 km. Its effect provided a temperature of 400°C in the San Pompeo 2 borehole (at a depth of 3000 m). Drilling in this region also revealed the presence of a deep permeable horizon in the basement separated by a thick impermeable stratum (600 m) from the main productive horizons. The rubidium-strontium and potassium-argon methods gave an age of the basement rocks within 2.5-3.7 million years [32]. Thermal waters and steam are confined to deposits of the Tuscan series — Triassic-Jurassic limestones. The gas content in the steam reaches 5.5% with the following composition: 93.0% CO_2 , 2.4% H_2S , 1.8% H_2 , 1.8% CH_4 , 1.0% N_2 . The typical composition of the calcium-sodium-magnesium bicarbonate water is represented by Perla Spring (M 1.83 g/liter; θ 0.92) [5]. The role of the magmatogenic component is estimated by the value of the helium isotope tracer $0.45 \cdot 10^{-5}$ [32]. The age of the given geothermal system is $(269 \pm 54) \cdot 10^3$ years. The hydrothermal waters and steam of Zephyria are clearly of thalassogenic feeding and were formed $30,000 \pm 6000$ years ago. In the Himalayas the highly thermal freshwater Manikaran Spring has an age of 7000 years, its gas composition is represented mainly by carbon dioxide (98.4%), hydrogen sulfide (0.6%), nitrogen (0.7%), and methane and hydrogen (traces) [35].

Hydrothermal fluids of volcanic belts of island arcs were studied within the Kuril-Kamchatka, Japan, and New Zealand segments. In the territory of Kamchatka most investigations were conducted within the limits of the Mutnovsk geothermal field [17, 25]. The Paratunka suite (Lower Miocene), represented by tuffs, tuff breccias, and propylitized lavas of andesite-basaltic composition, is the reservoir of hydrothermal fluids and steam. The maximum temperature of deep zones of the field is about 280°C , on the surface in the productive steaming boreholes it reaches 222°C . Three thermohydrodynamic complexes are identified in the section: upper single-phase, liquid phase; middle two-phase, vapor-liquid; and lower single-phase, high-temperature liquid. The first complex is tapped in the interval of absolute elevations +800 to +400 m. The geothermal gradient here decreases downward from 0.9 to $0.6^{\circ}\text{C}/\text{m}$, the formation pressure gradient varies from 0.0078 to $0.0100 \text{ MPa}/\text{m}$. The average mineralization of the fluid is 0.9 g/liter, the average value of the cation coefficient is 3.15. The base of the second complex corresponds to elevation -80 m. The geothermal gradient over the section decreases from 0.6 to $0.3^{\circ}\text{C}/\text{m}$, and the pressure gradient varies from 0.0048 to $0.0058 \text{ MPa}/\text{m}$. In the lower complex at a depth of 1500 m the geothermal gradient is $0.19^{\circ}\text{C}/\text{m}$ and the pressure gradient in the 1400-2100 m interval increases from 0.0059 to $0.0070 \text{ MPa}/\text{m}$. To estimate the age of the Mutnovsk geothermal system we used the hydrogeochemical data of the most studied upper complex under the assumption that the corresponding value of the coefficient θ differs little from the value characteristic for the lower complex. This problem is rather basic, since only the upper part of the geothermal field has been investigated by drilling and, furthermore, information on surface outflows is enlisted. However, of greatest interest is the time of formation of precisely the deep-seated source of the hydrothermal fluids, and the formula of the method (2) gives the best results at temperatures of more than 200°C (473°K). L. A.

Basharina [1] gives the composition of gas condensates from basaltic lavas of the Belyakin subordinate vent of the Klyuchevka volcano on the basis of samples taken in the temperature interval 680-102°C. We will compare the values of M and θ for various temperatures, 0°, C:

$T, ^\circ\text{C}$	680	500	360	210	102
g/liter	8,91	9,78	4,09	0,39	0,22
θ	1,97	2,61	1,12	0,79	0,91

As we see, mineralization of the fluid decreases 40-45 times and the cation coefficient by 2-3 times with decrease of temperature. If we take into account that the coefficient θ in formula (2) is taken in a logarithmic scale, then the difference will be 1.3-1.5 times. The latter fits into the root-mean-square error of the method (40%) in a predictive estimate of the unrevealed depths. The indicated tendency is manifested also in the chemical composition of the thermal springs of the Calabozos Caldera [30]. In the mouth temperature interval 50-96°C mineralization varies from 0.64 to 2.15 g/liter and the cation coefficient from 2.00 to 3.42. These conclusions are confirmed by the hydrochemical calculations of V. A. Il'in (1983), V. K. Saxena and M. L. Gupta (1985), and J. L. Bischoff and R. J. Rosenbauer (1989). On the basis of the given considerations, the age of the Mutnovsk hydrothermal system is determined to be $(124 \pm 25) \cdot 10^3$ years. The heat carrier of the given system is meteoric waters, which, as A. I. Serezhnikov et al. suggest [25], to judge from the characteristics of their isotopic composition form at elevations exceeding the hypsometric level of surface hydrothermal manifestations by 1.0 km, i.e., within the massif where the ancient Gorelyi volcano is located. The chemical composition of the gases in the steam from borehole V-2 indicates a noticeable role of magmatogenic fluid: carbon dioxide (96.3%) and hydrogen sulfide (3.2%) markedly dominate, ammonia, nitrogen, hydrogen, H_3BO_3 , methane, fluorine, and arsenic are present. The gas composition of the North Mutnovsk area is the following, %: CO_2 80.1, H_2S 5.0, CH_4 1.0, H_2 3.4, N_2 7.5, $^3\text{He}/^4\text{He}$ $1.0 \cdot 10^{-5}$. The top of the magma chamber of the Mutnovsk volcano is predicted at a depth of 6 km.

The significance of thalassogenic waters is great in feeding the hydrothermal system of the Lower Kozheleva field [18]. In borehole 7 fresh bicarbonate waters ($\theta = 3.5$) are obtained to a depth of 800 m, fresh sulfate waters ($\theta = 1.9$) to a depth of 1200 m, and brackish chloride waters ($\theta = 2.4$) to the bottom. In other boreholes superheated chloride waters had still higher (up to 47 g/liter) mineralization. At a depth of 3 km the temperature of the hydrothermal fluids is presumed to be about 370°C and their age $193,000 \pm 77,000$ years.

The Pauzhetka field, having very large thermal potential and natural resources, formed comparatively recently — 18,000 years ago (see Table 1). Still younger are the thermal vents in the Lower Paratunka, Nachikinskoe, Nalychevskoe, and Uzon areas (3000-9000 years). The origin of spontaneous gases and thermal waters of the young Uzon ore-forming system was studied by I. P. Lugovo et al. on the basis of isotope data [16]. They established that deep-seated carbon and water that passed through the meteoric cycle predominate in the hydrothermal fluids of the Uzon caldera. Boiling sodium chloride solutions in which components of a magmatic origin are present emerge onto the surface in the axial zone of the thermal anomaly. Thus, the value of $^{87}\text{Sr}/^{86}\text{Sr}$ equal to 0.7046 was determined on the basis of the Éksperimental'nyi Spring.

On islands of the Kuril Ridge (Paramushir and Kunashir) the age of the thermal springs within the limits of the Ébeko, Mendelev, and Golovnin volcanoes varies from 4000 to 8000 years (see Table 1), and the Upper Jurassic springs are characterized by mainly thalassogenic feeding. In the gas composition of the Lower Mendelev Springs CO_2 dominates (88.0%), hydrogen sulfide (10.0%) and nitrogen (2.0%) are present, i.e., the effect of the magmatogenic fluid is clearly manifested.

The Arima, Onikobe, Tamagawa, Wakura, and Matsukawa geothermal systems have been studied in the territory of Japan (see Table 1). The Arima thermal brine is typically magmatogenic, the isotopic composition of which is quite characteristic: $\delta^{18}\text{O} = +8.0\text{‰}$, $\delta\text{D} = -25\text{‰}$, $^3\text{He}/^4\text{He} = 1.0 \cdot 10^{-5}$ [23, 37]. Furthermore, the gases consist of hydrogen (51.4%) and carbon dioxide (46.7%). The age of the brine according to a sample from a depth of 168 m is $12,000 \pm 2000$ years. The aquifer complex composed of Miocene green tuffs and marine sediments is characterized by the Obuki and Wakura springs ($T_\theta = 8000$ -10,000 years) and the hydrothermal fluids and steam of the Onikobe ($T_\theta = 67,000 \pm 13,000$ years) and Matsukawa ($T_\theta = 49,000 \pm 10,000$ years) fields. The gas of the latter contains CO_2 (81.8%), hydrogen sulfide (14.1%), and nitrogen (4.1%). The close age of the hydrothermal fluids ($37,000 \pm 7000$ years) was established at the Matsao field (Taiwan), in the gas of which is more CO_2 (92.0%) and less hydrogen sulfide (5.0%), methane (0.7%), hydrogen (0.8%), and nitrogen (1.5%) are present [10].

The nitrogen thermal waters of Indonesia are presented by the Chi Solok freshwater spring, its time of formation is about 5000 years ago.

Fumaroles in the crater of the andesite White volcano (New Zealand) can served as a typical representative of hydrogen sulfide–carbonate thermal waters closely related to volcanic gases [10]. Next to the Big Donald fumarole formed an acid crater lake, the brines of which have a mineralization of 97.3 g/liter and age of 3000 years.

The slightly mineralized carbonate hydrothermal waters and steam of the Wairakei field have clearly meteoric feeding and that same age (see Table 1). In the Taupo zone [31] a geothermal system is predicted at a depth of 5 km, the time of formation of which reaches $46,000 \pm 18,000$ years.

An investigation of certain hydrothermal and steam fields showed that two distinct dependences of the value of the geothermal gradient g ($^{\circ}\text{C}/\text{m}$) on the common logarithm of the depth of occurrence (H , m) exit.

The upper interval (two-phase vapor–liquid) is traced to a depth of about 1000 m and is characterized by the equation

$$g_1 = 2,062 - 0,61\lg H \pm 0,05g \quad (r = -0,996). \quad (3)$$

The calculation was made for five objects (Calabozos, Zephyria, Mutnovsk, Arima, Wairakei).

The lower interval is distinguished at depths of 1000-8000 m (predictive) and is described by the equation

$$g_{II} = 0,69 - 0,1571\lg H \pm 0,12g \quad (r = -0,883). \quad (4)$$

The data for the calculation were taken for 14 objects (Pluum, Salton Sea, Cerro Prieto, Reykjavik, Krabla, Cape Banza, Larderello, Zephyria, Mutnovsk, Lower Kozheleva, Pauzhetka, Onikobe, Matsukawa, Matsao).

Equation (4) made it possible to predict differently the temperature at a depth of 5 km in the Taupo zone. Thus, whereas its value in [31] is assumed equal to $\sim 350^{\circ}\text{C}$, according to our data it is substantially higher, up to 550°C .

In the I interval very high temperatures are provided exclusively due to convection of fluid from the magma chamber, in the II interval the conductive component of the heat flow plays a considerable role. Therefore, we can evaluate the contrast of hydrothermal anomalies in the upper part of the field if we take Eq. (4) as the background equation.

For example, the Arima area: $H = 168$ m; $t = 133^{\circ}\text{C}$; $t_b = g_{II}H + t_0$ (mean annual temperature); $g_{II} = 0.69 - 0.157 \cdot 2.225 = 0.341^{\circ}\text{C}/\text{m}$; $t_b = 72^{\circ}\text{C}$; $\Delta t = 133 - 72 = 61^{\circ}\text{C}$. For the areas: Bhuttayagudem $H = 180$ m; $\Delta t = 20^{\circ}\text{C}$; Calabozos $H = 500$ m, $\Delta t = 112^{\circ}\text{C}$; Wairakei $H = 500$ m, $\Delta t = 92^{\circ}\text{C}$; Mutnovsk $H = 900$ m, $\Delta t = 42^{\circ}\text{C}$. Consequently, in the Arima area the effect of convection from the magma chamber is 3 times higher than in the Bhuttayagudem area and 1.2 times higher in the depths of the Calabozos Caldera than in the Wairakei hydrothermal system.

Trace elements in hydrothermal fluids were determined by many investigations [2, 3, 10, 13-15, 23-25, 29-31, 34, 35, 38]. Their level of accumulation depends strongly on total mineralization. Therefore, it is expedient to characterize the trace-element composition of hydrothermal fluids according to the following groups: strong brines (Salton Sea, Atlantis II, Danakil), weak brines (Pluum, Cerro Prieto, Guaymas, Ahuachapan, TAG, Reykjavik, Arima, Onikobe, Matsao, Manus), and little-mineralized thermal waters (Mud Volcano, Sonoma, Krabla, Allalobeda, Cape Banza, South Meager Creek, Calabozos, Pauzhetka, Mutnovsk, Matsukawa, Manikaran, Wairakei). Strong high-thermal brines contain, mg/liter: K 2352-17,500, Li 5.5-215, Sr 57-400, B 830-2232, SiO_2 81-520, Fe 100-6170, Zn 100-1400, Mn 0.4-18.5, Cu 5-540. The accumulation coefficients of potassium $K_K = K \cdot 10^3/\text{M}$, lithium $K_{Li} = Li \cdot 10^3/\text{M}$, boron $K_B = B \cdot 10^3/\text{M}$, SiO_2 $K_{\text{SiO}_2} = \text{SiO}_2 \cdot 10^3/\text{M}$, manganese $K_{Mn} = Mn \cdot 10^3/\text{M}$ clearly increase with age of strong brines, which are formed as a result of dissolution and leaching of evaporite deposits by high-temperature fluid:

$$K_K = 0,535T_b + 7,4 \quad (r = 0,996); \quad (5)$$

$$K_{Li} = 0,00747T_b - 0,012 \quad (r = 0,986); \quad (6)$$

$$K_B = 0,0547T_b + 2,5 \quad (r = 0,988); \quad (7)$$

$$K_{\text{SiO}_2} = 0,0167T_b + 0,21 \quad (r = 0,990); \quad (8)$$

$$K_{Mn} = 0,0437T_b + 0,53 \quad (r = 0,991). \quad (9)$$

Weak-brine thermal waters contain, in mg/liter: K 626-5018, Li 29-60, Sr 2.3-6.3, B 66-721, SiO₂ 32-1666, Fe 0.2-148, Mn 4-55, Cu 0.002-0.13, Zn 0.1-49. With the exception of silica, the level of accumulation of trace elements is about an order lower.

The accumulation coefficients of potassium, lithium, silica, conversely, decrease with age of the high-temperature weak brines:

$$K_K = 65,5 - 0,427\theta \quad (r = -0,713); \quad (10)$$

$$K_{Li} = 1,76 - 0,95 \lg T_\theta \quad (r = -0,781); \quad (11)$$

$$K_{SiO_2} = 58,2 - 22,5 \lg T_\theta \quad (r = -0,632). \quad (12)$$

Little-mineralized thermal waters are mainly impoverished in trace elements, the concentrations of which vary, mg/liter: K 6-225, Li 0.02-14.2, Sr 0.05-1.4, B 1.5-117, SiO₂ 86-880, Fe 0.01-45, Mn 0.0007-0.9, Cu to 0.002, Zn 0.010-0.025. The fluid of the Matsukawa field stands out against this background by anomalously high quantities of boron (684 kg/liter) and iron (508 kg/liter) [10]. Here the andesite and dacite welded tuffs and andesites were subjected to hydrothermal alteration. Unlike other hydrothermal systems of the group, the fluid with a temperature of 250-280°C has a pH 3-4 and contains high concentrations of sulfates (500-1500 mg/liter), CO₂, and H₂S. Its effect leads to active acid leaching of rocks over the entire section and to the formation of kaolinite, quartz, alunite, anhydrite, gypsum, and pyrite in them.

In the little-mineralized hydrothermal waters the accumulation coefficients of potassium, lithium, and silica also decrease with increase of the age of the systems:

$$K_K = 53,3 - 0,27\theta \quad (r = -0,510); \quad (13)$$

$$K_{Li} = 4,42 - 2,4 \lg T_\theta \quad (r = -0,839); \quad (14)$$

$$K_{SiO_2} = 293 - 131 \lg T_\theta \quad (r = -0,801). \quad (15)$$

Evidently, the process of formation of new minerals as a result of hydrothermal alteration of the enclosing rocks, e.g., K-feldspar, K-micas, and others, is realized in cases of weak-brine and little-mineralized thermal waters. In proportion to the hydrothermal system a large part of the heat energy is transformed into chemical energy and absorbed during mineralization [8].

The chemical composition of the water and gases of mud volcanos of the Kerch-Taman region, northwestern Caucasus, eastern Georgia, Azerbaijan, western Turkmenia, and Sakhalin Island was studied by I. A. Lagnova and S. D. Gemp [12]. Total mineralization and values of the cation coefficient vary in wide limits: M = 5.8 g/liter (Astrakhanka, Shemakha-Kobystan region)-150 g/liter (Gek-Patlaugh, western Turkmenia) and $\theta = 4.0-4.3$ (Khadyrly, Kura region - Gladkovskii, western Kuban)-1012.5-1332.1 (Inchabel' and Cheilakhtarma, Shemakha-Kobystan region). As is known, the roots of mud volcanoes are confined to very great depths (7-12 km and more), where the temperatures usually are 270-320°C and the pressures exceed 100-160 MPa, i.e., are in the lower gas zone. The solubility of water in methane and carbon dioxide, which dominate at such depths, exceeds 0.3 mole fraction [11]. The pronounced selective character of solubility of mineralized water in hydrocarbons was established in a number of experiments. It can be assumed that sodium salts pass into the gas-vapor phase considerably more intensely than calcium salts. Therefore, initially the value of the cation coefficient can be anomalously high (up to 2000). Moreover, under near-surface conditions sodium sulfates as a result of bacterial reduction are transformed into sodium bicarbonates and carbonates and simultaneously the bulk of calcium and magnesium precipitate [27]. Enrichment of mud-volcano waters in soda occurs as a result of hydrolysis of sodium feldspars. The condensation and solution waters established more than 25 years ago in the depths of gas-condensate and oil fields [11] are characterized by the presence of sodium chlorides and bicarbonates with a small density of alkali-earth salts. Thus the formation waters of gas-condensate reservoirs of the Karadag, Yuzhnoe, Lokbatah, and Zyrya structures (Azerbaijan) at depths of 3600-4800 m are characterized by values of θ equal to 56-115 [22].

According to the data of V. V. Nelyubin (1985), the brackish waters of the gas-condensate reservoirs in the northern part of the West Siberian megabasin are also impoverished in calcium (θ up to 101.4-641.4). In the crater lake of the Gek-Patlaugh volcano the brine formed in connection with the solvent passing into the hydrocarbon phase during degassing of deep zones and by subsequent evaporation of the water under arid climate conditions [11].

Thus, for estimating the age of waters of mud volcanoes we can use formula (2) with $\theta_0 = 2000$. In this case, however, a fictitious age of the mud volcanoes is implied, since formula (2) is derived for fluids with a magmatic component. The formation of the effluent channel of the Tarkhan mud volcano (Kerch Peninsula) occurred at the Oligocene-Early Miocene boundary ($T = 25$ million years). In the opinion of E. F. Shnyukov (1979), the intrusion of rocks at depths of 7-8 km is observed here ($t \sim 270^\circ\text{C}$, $P \sim 110$ MPa). Consequently $(T_\theta = 0.85(8.26/2.11)) \cdot \log(2000/17.9)10^{100/543} = (10.4 \pm 4.2) \cdot 10^4$ years = $104,000 \pm 42,000$. The effect of the deep-seated gas-vapor fluid is not refuted by the isotopic composition of the water ($\delta D = -16\text{‰}$, $\delta^{18}\text{O} = +12.5\text{‰}$) [27] and chemical composition of the gas (91.7% CO_2 , 8.1% CH_4 , 0.2% N_2) [12].

The Gek-Patlaugh mud volcano is located on the Gogran'-Dag-Chikishlyar deep fault, the age of the conducting fractures is about 8 million years ($T = 800 \cdot 10^4$ years). The depth of its roots is about 7 km ([9] ($t \sim 190^\circ\text{C}$, $P \sim 80$ MPa)).

$$T_\theta = 0,53 \frac{3,56}{1,89} \lg \frac{2000}{12} 10^{\frac{100}{543}} = (3,6 \pm 1,5) \cdot 10^4 \text{ years} = 36 \pm 15 \text{ thousand years.}$$

The roots of the Bulla Peninsula mud volcano Yuzhnyi (Baku archipelago) are presumed at a depth of 11 km ($t \sim 290^\circ\text{C}$, $P \sim 150$ MPa), age of the conducting fractures about 7 million years ($T = 700 \cdot 10^4$).

$$T_\theta = 0,93 \frac{6,68}{3,36} \lg \frac{2000}{206,4} 10^{\frac{100}{543}} = (2,7 \pm 1,1) \cdot 10^4 \text{ years} = 27 \pm 11 \text{ thousand years.}$$

The waters and gases of Kobystan mud volcanoes (Western Sheitanud, Syundi, Cheilakhtarma) arrive along thrust faults from Cretaceous deposits from depths of 7-8 km [6]. The Cheilakhtarma fold is complicated by a longitudinal axial fracture that formed in the middle of the age of the productive stratum ($T = 8$ million years). A large mud volcano releasing a large amount of gas, viscous oil, and mineralized water is confined to it. Its fictitious age is not great:

$$T_\theta = 0,44 \frac{3,12}{2,21} \lg \frac{2000}{1332} 10^{\frac{100}{543}} = (0,2 \pm 0,1) \cdot 10^4 \text{ years} = 2 \pm 1 \text{ thousand years.}$$

The helium isotope tracer of the mud volcanoes of the South Caspian megadepression is three orders lower compared with the mantle tracer [6]. The content of methane is high (87.7-99.2%) and carbon dioxide small (0.2-9.1%) [12]. All this indicates a genetic relation between mud-volcano gases of the region and gases of the sedimentary cover.

The examined examples of determining the fictitious age of mud volcanoes show a rather close correlation between T_θ and $\log \theta$:

$$T_\theta = 106 - 32,9 \lg \theta \quad (r = -0,722). \quad (16)$$

Therefore, this equation should be recommended for a quick estimate of the fictitious age of mud volcanoes.

Mud-volcano waters contain trace elements, mg/liter: K 6-538, Sr 1-144, B 29-950, As 0.05-0.060, NH_4 0.1-67.7, Br 8-376, I 4-65 [12]. The accumulation coefficients of most trace elements display characteristic relations to the value of the cation coefficient in a logarithmic scale (Table 2), i.e., to the fictitious age of mud-volcano waters. The values of K_K , $K_{\text{Sr}} = (\text{Sr} \cdot 10^3)/M$, $K_{\text{B}/\text{HCO}_3} = (\text{B} \cdot 10^3)/\text{HCO}_3$, $K_{\text{NH}/\text{HCO}_3} = (\text{NH}_4 \cdot 10^3)/\text{HCO}_3$ increase rather clearly with age, which indicates passage of potassium, strontium, boron, and ammonium into the aqueous phase from the enclosing rocks. The directly opposite tendency is noted with respect to bromine and iodine (see Table 2). Thus, the values of the bromine-chlorine $(\text{Br} \cdot 10^3)/\text{Cl}$ and iodine-chlorine $(\text{I} \cdot 10^3)/\text{Cl}$ ratios decrease with time. This can be explained by processes of scattering, redistribution, equalization, and impoverishment of bromine and iodine concentrations as a result of molecular and convective diffusion, sorption, and degassing of waters.

The fictitious age of subsurface condensation and solution waters detected in the depths of gas-condensate and oil reservoirs [4, 7, 11] can be estimated analogously.

TABLE 2. Dependences of the Accumulation Coefficients of Trace Elements on the Age Index θ of Mud-Volcano Waters [12]

Regression equation	Number of objects	Correlation coefficient	Cation coefficient θ	
			500 $T_0 = 17 \cdot 10^3$ years	10 $T_0 = 73 \cdot 10^3$ years
$K_K = 6.43 - 1.89 \lg \theta$	32	-0.52	1.3	4.5
$K = 1.68 - 0.6 \lg \theta$	26	-0.66	0.06	1.08
$\lg K_{B/HCO_3} = 3.12 - 0.66 \lg \theta$	26	-0.51	21.8	288.4
$\lg K_{NH_4/HCO_3} = 2.70 - 0.92 \lg \theta$	29	-0.73	1.6	60.3
$K_{Sr/Cl} = 1.77 + 3.56 \lg \theta$	28	+0.47	11.4	5.3
$K_{I/Cl} = 4.15 \lg \theta - 3.0$	27	+0.48	8.2	1.2

Thus, the solution fluids of reservoirs of the Upper Cretaceous horizon of the Terek–Sunzha region (Él'dorovo, Oktyabr'sk, Starogroznensk) underlie thick oil accumulations as freshened water banks ($M = 1.62$ – 12.8 g/liter) and are characterized by θ values from 3.8 to 102.7 [4]. Vertical migration of the gas–vapor system, evidently, occurred from Upper Jurassic underlayer deposits from depths of 8–9 km along fractures of the Sredinnii fault that formed in the pre-Akchagylan folding phase ($T \sim 8$ million years). The maximum paleotemperatures determined by the thermobarogeochemical method exceeded 280°C [26], the formation pressures reached 120 MPa. The values of T_0 obtained vary from 40,000 to 84,000 years. The deep-seated hydrogeological inversion anomaly in deep zones of the Machekh gas field of the Dnepr-Donetsk depression [7], to judge from the values $\theta = 6.3$ (for M 3.1 g/liter), $t \sim 200^\circ\text{C}$, $P = 95$ MPa, and time of formation of the fault about 1 million years ago, has an age of $19,000 \pm 7000$ years. A distinctive feature of the condensation waters of this field is anomalous enrichment in iron ($\text{Fe} \cdot 10^3$)/ $M = 177.9$, which even exceeds the concentration of this metal in fluids of the Matsukawa geothermal field (118.1).

Thus the examined material indicates the applicability of the kinetic-geochemical method for estimating the age of hydrothermal fluids in volcanic regions, rift zones, island arcs, mud-volcano waters, and condensation and solution waters of deep hydrocarbon accumulations.

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METHODS

PROCEDURE FOR DETERMINATION AND THE SIGNIFICANCE OF WATER IN MINERALS

A. A. Nyrkov

UDC 550.5:556.08

Study of the water contained in minerals is of great theoretical and practical significance. Of the total number of mineral species (~ 2000), 54% contain water or water-bearing components H_nO (with $n = 1, 2, 3$). In particular, in such groups as phosphates, sulfates, borates, and silicates the portion of water-bearing minerals is 92, 87, 73, and 67%, respectively. Half of the mineral species belong precisely to these four groups (three quarters of the mass of the Earth's crust). In the Earth's sedimentary mantle, water-containing minerals amount to no less than 13%, and they contain $4.8 \cdot 10^{16}$ tons of water, which is four times more than in all the rivers and oceans of the world. The water in minerals participates in the cycle, being released as a result of metamorphism and absorbed as a result of hypogene processes.

In mineralogy, the following classification of water in minerals has been established: constitutional, crystallization, adsorbed, and the water of inclusions. One kind of water is usually present in a mineral, while two or three are clearly noted in some, and at times even all four kinds. In hydromicas, for example, at least three crystal-chemical types of water are known: adsorption-molecular, constitutional-hydroxyl $2(OH) \rightarrow H_2O + O$, and interlayer. They occupy different positions in the structure of water-containing minerals and are retained there with different strengths. Other possible types of water in minerals are also not ruled out.

Meanwhile, the procedure for investigating water in minerals is imperfect. So far, the analytic chemist is limited to showing H_2O^- and H_2O^+ . What is more, there are frequent cases when it is not water that is shown as H_2O^- and H_2O^+ , but weight loss in drying or calcination. It is easy to understand that this is not the same thing, if organic matter, lower-oxide compounds, sulfides, or carbonates are present in the sample.

In some cases, researchers get dehydration curves by collecting and weighing the water released by heating through $100^\circ C$, or they judge it from the density of water vapor or according to data from gas volumetric analysis. We have already spoken out [3, 4, 8] against unrepresentative results "for water" in analyses and suggest a procedure for separate determination of the different crystal-chemical types of water. For this purpose, we tested a simple homemade instrument on hydromicas, which makes it possible not only to determine, but also to collect liquid water of three types.

The design of the instrument consists of a steel reaction vessel and a glass condenser connected by a steel tube 300 mm long, with inside diameter of 4 mm. The sample is put into the reaction vessel and the back lid is bolted shut. A repeatedly calcined asbestos or copper gasket can be used for tighter sealing. The temperature is monitored by a Chromel-Alumel thermocouple. The glass condenser with running water should have a length that guarantees complete condensation of water vapors (no less than 300 mm). Dripping water is collected in a calibrated test tube. With the help of such an instrument, a quantitative representation of three types of water in hydromicas was obtained (Figs. 1 and 2).

Our tests with sericite and glauconite showed good agreement with thermographic data. Low-temperature molecular water was collected by holding the sample at $180^\circ C$ for 2 h. During this time, the sample "dries out," and a subsequent rise in temperature to $350^\circ C$ does not produce a single drop of water. At $350^\circ C$, interlayer water begins to be released. Holding the temperature at $420^\circ C$ makes it possible to completely collect the interlayer water. After that, the temperature is raised to $650^\circ C$, and release of the third type of water begins approximately from $480^\circ C$. This method of dehydration with the use of samples weighing 200-300 g made it possible to collect a sufficient amount of the different types of water for subsequent study of their isotopic composition.

The nature of these three types of water H_nO in hydromicas was clarified with varying degrees of reliability. With $n = 2$, we get molecular water, which constitutes the whole set of adsorption, film, colloidal, capillary, and hygroscopic water. With $n = 1$, we get hydroxyl water. It is securely held in the lattice and is released from silicates at $450-800^\circ C$.

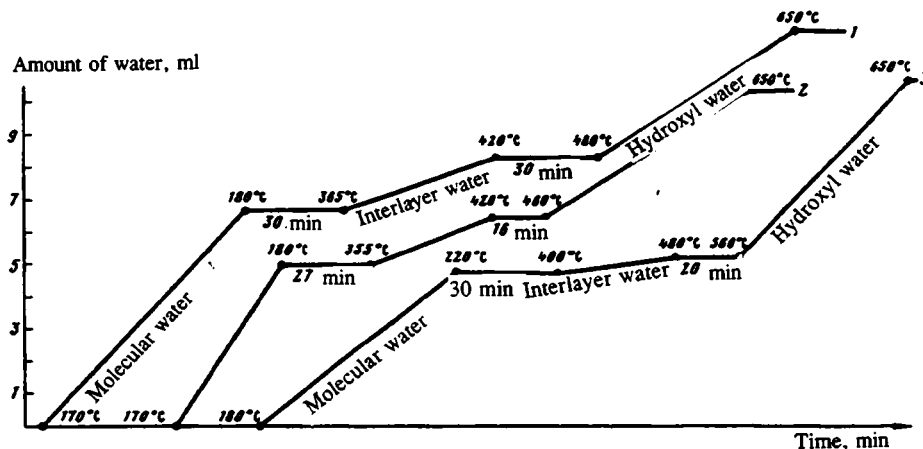


Fig. 1. Kinetics of release of water from hydromicas with heating in stages: 1, 2) glaucanites, Nizhnezhuravsk and Kryukov, respectively; 3) sericite.

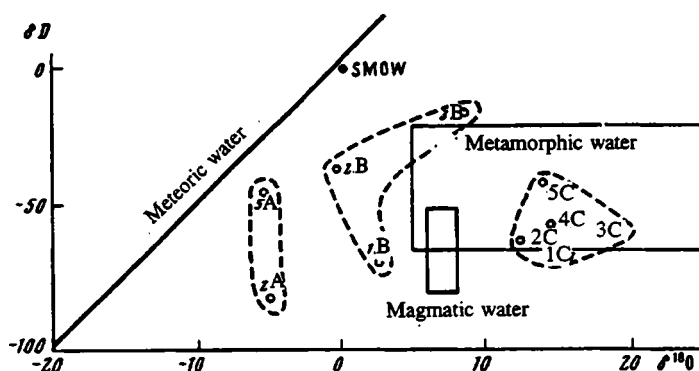


Fig. 2. Isotopic composition of different types of water in hydromicas (A – adsorbed, B – interlayer, C – hydroxyl). 1-5) specimen numbers (see Table 1).

With $n = 3$, we get problematic oxonium, in relation to which debate still continues. Quite a few investigations have been devoted to this question [1, 2, 5, 6, 9, 12], however no unified point of view has been worked out yet on the nature of interlayer water.

The composition and properties of the three types of water contained in the same specimen of hydromicas are not the same (see Fig. 2 and Table 1). This makes it possible to get additional crystal-chemical and genetic information. The point is that the reactivity to ion exchange of water contained in minerals varies depending on its structural position. The most strongly retained hydroxyl water is "hidden" as it were inside the crystal lattice in the form of OH^- ions and therefore is less subject to isotopic exchange than other types. Consequently, the isotopic composition of oxygen and hydrogen in hydroxyls is preserved to a greater degree as it was in the environment of the mineral's origin. Other types of water (adsorbed, interlayer) probably had the same isotopic composition at that time. However, subsequent contact of the mineral with another water environment can lead to a situation in which interlayer and, especially, adsorption waters acquire different values for deuterium and oxygen-18.

The most diverse variations in amount of deuterium and oxygen-18 are conceivable. In contemporary exogenous hydromicas that arose as a result of synthesis, all three kinds of water can be the same in isotopic composition, if the conditions in which they arose did not undergo significant changes. Endogenous hydromicas to some degree inherit the isotopic indices of magmatic waters, but most often they show dilution of these waters with meteoric or underground ones.

TABLE 1. Isotopic Composition of Various Types of Water, %

Specimen number (see Fig. 2)	Minerals	Type of water		
		Adsorption	Interlayer	Hydroxyl
1	Nizhnezhuravsk glauconite	—	$\frac{-69}{+2,8}$	$\frac{-67}{+14,8}$
2	Kryukov glauconite	$\frac{-82,4}{-4,9}$	$\frac{-36,4}{-0,2}$	$\frac{-61,5}{+12,5}$
3	Kryukov glauconite (fraction)	—	$\frac{-15}{+8,5}$	$\frac{-5,7}{+19,5}$
4	Verkhnedula glauconite	—	—	$\frac{-56}{+14,2}$
5	Khudes sericite	$\frac{-44,5}{-5,3}$	$\frac{-44,5}{\text{Not found}}$	$\frac{-39}{+13,9}$

In our case, glauconite from sedimentary deposits of Tertiary age contains three kinds of water differing in their contents of deuterium and oxygen-18. Consequently, the glauconite experienced a complex history from the time of its formation. According to its isotopic composition on a Taylor diagram (see Fig. 2), hydroxyl water falls into the field of "endogenous" waters, while interlayer and molecular waters have reduced values of oxygen-18 and lie outside of the "endogenous rectangle," approaching the line for meteoric waters.

The genetic interpretation of the data seems to be as follows. The glauconite was formed in a sea with underwater volcanic eruption, i.e., at the time of the glauconite's origin magmatic and sea waters could have participated in formation of its composition and were securely fastened in the crystal lattice in the form of OH. It is possible and even likely that at that time the same waters also took part in formation of other oxygen-hydrogen groupings, however the latter came into contact with other types of water and were subjected to isotopic exchange in the course of the glauconite's dispersion over the sea bottom, diagenesis, catagenesis (late stage of diagenesis), and hypergenesis. The interlayer water has traces of isotopic exchange during diagenesis in marine conditions; and the molecular water reflects the action of underground and meteoric waters during hypergenesis.

In contrast to glauconite, sericite from the Khudes pyrite deposit shows the same or close values of deuterium for the three types of water, but it has differences in oxygen-18. It is known [10,11] that the main feature of the computed isotopic compositions of most hydrothermal solutions is that a very wide range of change in amounts of $\delta^{18}\text{O}$ is observed in deposits, with quite insignificant variations in δD . This is precisely the pattern that is characteristic of the Khudes sericite from altered rocks surrounding ores. There, the hydroxyl water is also in the field of endogenous waters (magmatic and metamorphic), while the molecular water, as expected, is close to the lines of meteoric waters because the specimen stayed for some time in the zone of hypergenesis. The usefulness of such analyses for clarifying the genesis of minerals raises no doubt [6]. What is more, not all of the possibilities of isotopic mineralogical investigations have been used yet. In particular, we can count on additional genetic and crystal-chemical information if we provide for separate determination of the isotopic composition of oxygen in hydroxyls and in silicon-oxygen tetrahedra in the same mineral. At present, a new scientific direction is forming: isotopic mineralogical, in contrast to the already existing isotopic lithological one [7]. The different possibilities of these directions bring about the need for different methodological approaches to preparation of samples for isotopic analysis.

Study of water in minerals links such sciences as mineralogy, crystal chemistry, hydrochemistry, teaching about mineral resources, ecology, etc. and can have great applied significance.

So, clarification of the types of water in minerals, their composition and position in the crystalline structure, and the dependence of the water's composition on genesis, age, experimental conditions, etc. raises a number of important scientific and practical problems. One of them is provision of mankind with clean water, of which there is none in rivers or oceans. It is also not known where to get clean water, if only in limited amounts for scientific purposes. True, it is not ruled out that in the future enormous volumes of water will be obtained in this way. This question is particularly urgent for desert regions and extreme situations. Production of clean water by distillation of polluted water solves the problem only partially, since some pollutants evaporate together with water vapors. Isolation of pure water from minerals by means of heat treatment seems preferable to us, although isolation of water by other means is also possible. It is logical to expect that OH water in ancient minerals is the purest, however there has been no purposeful research in this direction.

Another prospective problem that is also presently unresolved is study of the question of whether minerals of ultrabasic, acidic, and alkali magmatic rocks contain water with the same or different composition. Is it possible, like fauna for sedimentary rocks, to use the isotopic composition of some type of water for identification, say, of granites from one magmatic chamber?

The list of these questions can be continued. How does the isotopic composition of OH water in the same mineral depend on age and genesis? How do different types of water behave in minerals at low and superlow temperatures? Is ice of different types of water the same in structure, transition temperature, etc.? How do different types of water in ancient minerals affect a living organism? The answers to these and other such questions are of scientific and practical interest, and there is apparently an urgent need to organize purposeful research in this field.

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SHAFAYAT FARKHAD OGLY MEKHTIEV

**M. T. Abasov, Ak. A. Ali-Zade, É. Sh. Shikhalibeili, V. N. Kholodov,
Z. A. Buniat-Zade, and Yu. K. Burlin**

On December 15, 1993, at the age of 83, the prominent Soviet petroleum scientist, Academician of the Academy of Sciences of the Azerbaidzhani Republic, corresponding member of the International Commission of the History of Geological Sciences (INHIGEO), honorary oil worker of the USSR, honorary worker of the gas industry of the USSR, honored scientist of Azerbaidzhan, winner of the State prize, doctor of geological and mineralogical sciences, Professor Shafayat Farkhad ogly Mekhtiev died.

A graduate of the mining department of the Azerbaidzhani Oil Institute, Sh. F. Mekhtiev had worked in the oil industry since 1933. From the first days of the Great Patriotic War, officer Sh. F. Mekhtiev defended the motherland with a weapon in his hands.

Called away from the front in 1944 as a petroleum specialist, in 10 years of work at the Institute of Geology of the Academy of Sciences of Azerbaidzhan he defended his candidate's and doctoral dissertations, progressed from graduate student to director, and was selected as corresponding member (1953) and then full member (1958) of the republic's Academy of Sciences.

In 1958-1965, he was rector of the Azerbaidzhani State University, and from 1965 until his death he headed the division of oil and gas geology of the Institute of Geology of the Academy of Sciences of Azerbaidzhan (IGANA) and was chairman (until 1970) and then professor of the department of geology and exploration of oil and gas fields.

In his sixty years of scientific, organizational, pedagogical, and production activity, Sh. F. Mekhtiev left a deep mark on all of these fields.

His half a century of scientific research encompassed fundamental critical problems of modern oil and gas geology, on many of which he obtained unique results that were more than once included by resolutions of the Presidium of the Academy of Sciences of the USSR among the most important achievements of Soviet science. This is clear from just two examples.

Thus, in the fundamental problem of the genesis of oil, which has been debated for a century, Sh. F. Mekhtiev put forth an original hypothesis of its deep biogenic origin, which he subsequently refined to the level of a theory that is finding acceptance among a growing number of domestic and foreign specialists as quite promising and the one that most fully corresponds to the current level of our knowledge.

Another example can be the "Map of Oil and Gas Fields and Promising Structures of the Azerbaidzhani SSR" on a scale of 1:500,000, with detailed explanatory notes, which was compiled under his scientific editorship in 1985, had no analog in the whole Soviet Union, and was highly regarded by leading Soviet scientists.

More than 400 scientific works published in recognized scientific centers of the Soviet Union and more than 10 foreign countries belong to the pen of Sh. F. Mekhtiev.

His program reports on critical problems of oil and gas geology, which he gave many times at world and international petroleum and geological forums in Australia, Bulgaria, Hungary, India, Canada, Mexico, the USA, France, West Germany and other countries, earned widespread recognition from the world geological community.

From his student years until the last days of his life, Academician Sh. F. Mekhtiev carried out a great deal of pedagogical work, teaching special courses at higher educational institutions in Baku on a number of modern disciplines of oil and gas geology and geochemistry. Today his students work on many continents. He created the "Mekhtiev school," which is recognized in oil geology and numbers about 100 doctors and candidates.

Sh. F. Mekhtiev was distinguished by breadth of vision; he always cared about the growth of young scientists, and he himself actively generated new ideas and was the initiator of development of new directions in science. The dedicated work of Shafayat Farkhadovich and his associates helped to establish Baku as one of the leading centers of oil geology.

Editorial staff of the journal *Litologiya i Poleznye Iskopaemye*; Interdepartmental Lithological Committee of the Russian Academy of Sciences. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 140-141, July-August, 1994.

The geological community of all republics of the former Soviet Union and many foreign countries knew Sh. F. Mekhtiev as the organizer of a number of major (including international) conferences and seminars on the most controversial and critical problems of oil and gas geological science and practice, at which he himself invariably gave the keynote addresses.

Sh. F. Mekhtiev deservedly enjoyed universal recognition and deep respect among his colleagues — the geologists and petroleum specialists who were fortunate enough to communicate with him.

The bright image of this prominent scientist, talented teacher, and outstanding person will live in the hearts of his friends, students, and comrades.

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